(43) Publication Date: January 23, 2001

(51) Int. Cl.[7]: C03B 20/00

8/04

C03C 3/06

H01S 3/17

3/30

C03B 20/00

8/04

C03C 3/06

H01S 3/17

3/30

Theme (reference): F 4G014

G 4G062

R 5F072

F Code (reference): 4G014 AH15

4G062 AA04 BB02 DA01 DA10 DB01

DC01 DD01 DE01 DF01 EA01

EA10 EB01 EC01 ED01 EE01

EF01 EG01 FA01 FA10 FB01

FC01 FD01 FE01 FF01 FG01

FH01 FJ01 FD01 FL01 GA01

GB01 GC01 GD01 GE02 HH01

HH03 HH05 HH07 HH09 HH11

HH13 HH15 HH17 HH20 JJ05

JJ06 KK01 KK03 KK05 KK07

KK10 MM02

5F0072 AA04 AA06 FF07 FF08 JJ03

RR05 YY08

No. of Claims: 18 (Total of 25 pages; OL)

Examination Request: Not requested

(21) Application No.: Hei 11[1999]-307783

(22) Application Date: October 28, 1999

(30) Priority Data

(31) No.: Hei 10[1998]-307476

(32) Date: October 28, 1998

(33) Country: Japan

(31) No.: Hei 10[1998]-338636

(32) Date: November 30, 1998

(33) Country: Japan

(31) No.: Hei 10[1998]-350116
(32) Date: December 9, 1998
(33) Country: Japan
(31) No.: Hei 10[1998]-353339
(32) Date: December 11, 1998
(33) Country: Japan
(31) No.: Hei 10[1998]-353351
(32) Date: December 11, 1998
(33) Country: Japan
(31) No.: Hei 10[1998]-367671
(32) Date: December 24, 1998
(33) Country: Japan
(31) No.: Hei 10[1998]-370014
(32) Date: December 25, 1998
(33) Country: Japan
(31) No.: Hei 11[1999]-93613
(32) Date: March 31, 1999
(33) Country: Japan
(31) No.: Hei 11[1999]-275030
(32) Date: September 28, 1999
(33) Country: Japan

(71) Applicant: 000000044
 Asahi Glass Co., Ltd.
 1-12-1 Yuraku-cho, Chiyoda-ku, Tokyo-to
(72) Inventor: [illegible] Ikuta
 Asahi Glass Co., Ltd.
 1150 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa-ken
(72) Inventor: Nobuya Kikugawa
 Asahi Glass Co., Ltd.
 1150 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa-ken
(72) Inventor: Noriaki Shimodaiara
 Asahi Glass Co., Ltd.
 1150 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa-ken
(72) Inventor: Akeo Masui
 Asahi Glass Co., Ltd.
 1150 Hazawa-cho, Kanagawa-ku, Yokohama-shi, Kanagawa-ken
(72) Inventor: Shuhei Yoshizawa
 Asahi Glass Co., Ltd.
 2-1-2 Murunouchi, Chiyoda-ku, Tokyo-to
(74) Agents: 100080159
 Mochinari Watanabe, patent attorney, and 1 other

[There are no amendments to this patent.]

(54) SYNTHETIC QUARTZ GLASS AND ITS MANUFACTURING METHOD

(57) ABSTRACT

Purpose: To provide synthetic quartz glass in which the E' center and fluorescent light emission are reduced.

Solution means: Synthetic quartz glass in which fluorine is included; the value (I_{2250}/I_{800}) of the scattering peak intensity I_{2250} of 2250 cm^{-1} to the scattering peak intensity I_{800} of 800 cm^{-1} in a laser Raman spectrum is 1×10^{-4} or less, and the absorption coefficient of light of 245 nm is 2×10^{-3} cm^{-1} or less.

CLAIMS

1.   Synthetic quartz glass, characterized by the fact that in optical synthetic quartz glass used by irradiating light of the ultraviolet region to the vacuum ultraviolet region, fluorine is included, the ratio (I_{2250}/I_{800}) of the scattering peak intensity I_{2250} of 2250 cm^{-1} to the scattering peak intensity I_{800} of 800 cm^{-1} in a laser Raman spectrum is 1×10^{-4} or less, and the absorption coefficient of light of 245 nm is 2×10^{-3} cm^{-1} or less.

2.   The synthetic quartz glass of Claim 1, characterized by the fact that the fluorine concentration is 100 ppm or more.

3.   The synthetic quartz glass of Claim 1 or 2, characterized by the fact that the OH group concentration is 100 ppm or less.

4.   The synthetic quartz glass of any of Claims 1-3, characterized by the fact that the chlorine concentration is 100 ppm or less.

5.   The synthetic quartz glass of any of Claims 1-4, characterized by the fact that the ratios I_{495}/I_{440} and I_{606}/I_{440} of the scattering peak intensity I_{495} of 495 cm^{-1} and the scattering peak intensity I_{606} of 606 cm^{-1} to the scattering peak intensity I_{440} of 440 cm^{-1} in the laser Raman spectrum are respectively 0.585 or less and 0.136 or less.

6.   The synthetic quartz glass of any of Claims 1-5, characterized by the fact that the OH group concentration is 50 ppm or less.

7.   The synthetic quartz glass of any of Claims 1-5, characterized by the fact that the OH group concentration is 10 ppm or less.

8.   ·The synthetic quartz glass of any of Claims 1-5, characterized by the fact that in the synthetic quartz glass for an optical part used in a wavelength band of 160 nm or less, the OH group concentration is 5 ppm or less.

9.   The synthetic quartz glass of any of Claims 1-8, characterized by the fact that the virtual temperature is 1,100°C or less.

10.   The synthetic quartz glass of Claim 8 or 9, characterized by the fact that the internal transmittance at a wavelength of 157 nm is 80%/cm or more.

11.   Synthetic quartz glass, characterized by the fact that in optical synthetic quartz glass used by irradiating light of the ultraviolet region to the vacuum ultraviolet region, it is formed from synthetic quartz glass containing the OH group and fluorine; the extent* of the OH group concentration in the optical operation region is 15 ppm or less; the extent of the fluorine concentration is 15 ppm or less; and the chlorine concentration is 25 ppm or less.

12.   Synthetic quartz glass, characterized by the fact that in an optical synthetic quartz glass containing an OH group used by irradiating light of the ultraviolet region to the vacuum ultraviolet region, it is formed from a synthetic quartz glass containing the OH group and fluorine; the extent of the OH group concentration in the optical operation region is 25 ppm or less; the extent of the fluorine concentration is 25 ppm or less; and the chlorine concentration is 25 ppm or less.

13.   The synthetic quartz glass of Claim 11 or 12, characterized by the fact that the extent of the fluorine concentration and the extent of the OH group concentration in the optical operation region is 5 ppm or less.

14.   The synthetic quartz glass of any of Claims 11-13, characterized by the fact that the refractive index variation (Δn) in a plane orthogonal to incident light is 20×10^{-6} or less.

15.   The synthetic quartz glass of any of Claims 11-13, characterized by the fact that the refractive index variation (Δn) in a plane orthogonal to incident light is 5×10^{-6} or less.

16.   A method for manufacturing synthetic quartz glass, characterized by the fact that in a method for manufacturing synthetic quartz glass used by irradiating light of the ultraviolet region to the vacuum ultraviolet region, it includes (a) a process that forms a porous quartz glass by depositing and growing fine quartz glass particles, which are obtained by flame-hydrolyzing a raw material for forming the quartz glass, on a base material, (b) a process that holds the porous quartz glass in an atmosphere containing fluorine and obtains a porous quartz glass containing fluorine, and (c) a process that transforms the porous quartz glass containing fluorine into transparent glass by heating up to the transparent glass formation temperature and obtains transparent quartz glass containing fluorine.

17.   The method for manufacturing synthetic quartz glass of Claim 16, characterized by the fact that in process (b), a gas containing fluorine is introduced in a state in which the temperature is held at lower than 600°C under reduced pressure, so that the atmosphere containing fluorine is formed.

18.   The method for manufacturing synthetic quartz glass of Claim 16 or 17, characterized by the fact that the following process (e) is further applied between processes (b) and (c):

---

* [Editor's note: Japanese text literally stated "variation width," which was interpreted to merely mean the extent or level of concentration.]

(e) a process that decompresses the atmosphere and holds the porous quartz glass for a prescribed time under reduced pressure.

DETAILED EXPLANATION OF THE INVENTION

[0001]
TECHNICAL FIELD OF THE INVENTION

The present invention pertains to synthetic quartz glass, which is used in an optical part of a device having ultraviolet rays with a wavelength of 400 nm or less as light source, along with its manufacturing method. More specifically, it pertains to synthetic quartz glass, which is used as an optical part (including products or half-finished products) such as a lens (projection system and illumination system), used in light from the ultraviolet region to the vacuum ultraviolet region emitted form light sources such as an excimer laser (XeCl: 308 nm, KrF: 248 nm and ArF: 193 nm), F_2 laser (157 nm), low-pressure mercury lamp (185 nm), Xe_2 excimer lamp (173 nm), and heavy hydrogen lamp (110-400 nm), prism, etalon, photomask, pellicle (pellicle material, pellicle film, or both of them), and window material, along with its manufacturing method.

[0002]
PRIOR ART

The synthetic quartz glass is characterized by being a transparent material over a wide wavelength band from the near-infrared region to the vacuum ultraviolet region, having a very small thermal expansion coefficient and excellent size stability, seldom containing metal impurities, and having a high purity. For this reason, the synthetic quartz glass has been mainly used in optical parts for conventional optical devices using g-rays (436 nm) and i-rays (365 nm) as light sources.

[0003]

Recently, along with a high integration of LSIs, in photolithography for image-drawing an integrated circuit pattern on a wafer, a fine image drawing technique having a finer line width has been in demand, and in response to such a demand, shortening of the wavelength of the exposed light source is in progress. For example, as light source of a stepper for lithography, instead of the conventional g-ray and i-rays, a KrF excimer laser and an ArF excimer laser are used; also, a F_2 laser is expected to be used.

[0004]

Also, the low-pressure mercury lamp, Xe_2 excimer lamp, and heavy hydrogen lamp are used: 1) in apparatuses such as optical CVD, 2) silicon wafer ashing apparatus or etching apparatus, or (3) ozone generator, etc., and their development is in progress to apply them to the photolithography technique in the future. In gas-sealed tubes used in the low-pressure mercury lamp, excimer lamp, heavy hydrogen, etc., in optical devices using the above-mentioned short-wavelength light source, and in optical parts used by irradiating their short-wavelength light, it is also necessary to use the synthetic quartz glass.

[0005]

In the synthetic quartz glass used in these optical parts, optical transmittance at a wavelength from the ultraviolet region to the vacuum ultraviolet region is required, and it is in demand that the transmittance not be lowered by the ultraviolet irradiation (hereinafter, simply called "ultraviolet ray resistance"). Also, in optical parts used by irradiating light from the ArF excimer laser, F_2 laser, low-pressure mercury lamp, Xe_2 excimer lamp, heavy hydrogen lamp, etc., it is in demand that the optical transmittance in the vacuum ultraviolet region at a wavelength of 200 nm or less (hereinafter, simply called "vacuum ultraviolet ray transmittance") should be excellent. Also, in optical parts used in light with a wavelength of 200 nm or less, it is in demand that the refractive index variation (Δn) be smaller (hereinafter, called "homogeneity") than conventional values.
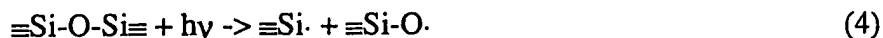
[0006]

In conventional synthetic quartz glasses, for example, when high-energy light emitted from light source such as the KrF excimer laser and ArF excimer laser was irradiated, a new absorption band was generated in the ultraviolet region, so that they had problems as optical parts in constructing an optical system using ultraviolet rays as light source. In other words, when the ultraviolet rays are irradiated for a long time, an absorption band of about 215 nm called the so-called E' center ($\equiv Si\cdot$) and an absorption band of about 260 nm called the NBOHC (noncrosslinked oxygen radical: $\equiv Si\text{-}O\cdot$) are generated.

[0007]

There are basically two reasons why these absorption bands are generated. One is due to a structural defect in the synthetic quartz glass, that is, $\equiv Si\text{-}Si\equiv$ (oxygen deficiency type defect), reduction type defect such as $\equiv Si\text{-}H$, or oxidation type defect such as $\equiv Si\text{-}O\text{-}O\text{-}Si\equiv$, and the other is due to an unstable structure in the synthetic quartz glass, that is, a three-parted ring structure and four-parted ring structure. These defects are eliminated by the ultraviolet irradiation as shown in the following equations (1)-(4), so that paramagnetic defects (E' center and NBOHC)

are generated. It is considered that if the paramagnetic defects exist, the decrease in the transmittance, the decrease in the ultraviolet ray resistance, increases in the absolute refractive index, the variation of the refractive index profile, and fluorescence are generated.

[0008]

$$\equiv Si\text{-}Si\equiv + h\nu \rightarrow 2\equiv Si\cdot \tag{1}$$

$$\equiv Si\text{-}H + h\nu \rightarrow \equiv Si\cdot + H\cdot \tag{2}$$

$$\equiv Si\text{-}O\text{-}O\text{-}Si\equiv + h\nu \rightarrow \equiv Si\cdot + O\cdot \tag{3}$$

$$\equiv Si\text{-}O\text{-}Si\equiv + h\nu \rightarrow \equiv Si\cdot + \equiv Si\text{-}O\cdot \tag{4}$$

[0009]

In order to solve these problems, various methods have been reviewed, and it is known that hydrogen molecules may be included in a certain form in the synthetic quartz glass. For example, in Japanese Kokai Patent Application No. Hei 3[1991]-88742, a method for suppressing the transmittance decrease due to the ultraviolet irradiation by including hydrogen molecules at 5×10^{16} molecules/cm^3 or more in the synthetic quartz glass and including OH groups at 100 ppm or more is presented.

[0010]

However, in the OH groups of the synthetic quartz glass, the reaction of the following equation (5) was advanced by the ultraviolet irradiation, so that NBOHC was generated, there was an absorption of 260 nm, and a fluorescence of 650 nm was generated.

$$\equiv Si\text{-}OH + h\nu \rightarrow \equiv Si\text{-}O\cdot (NBOHC) + H\cdot \tag{5}$$
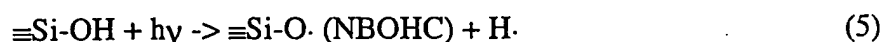
[0011]

Even if the hydrogen molecules were included, the reaction of equation (5) could not be completely prevented; in particular, when OH group concentration was high, the fluorescence of 650 nm was strong. Also, when the OH group concentration was high, since the transmittance of light at 150-180 nm was decreased, there was a problem when the synthetic quartz glass was used in devices having a low-pressure mercury lamp, Xe$_2$ excimer lamp, F$_2$ laser, etc., as light sources.

[0012]

In order to solve these problems, in Japanese Kokai Patent Application No. Hei 6[1994]-227827, synthetic quartz glass in which the OH group concentration is 10 ppm or less, the halogen concentration is 400 ppm or less, and hydrogen molecules are included is proposed.

Using this synthetic quartz glass, since the OH group concentration is low, the ultraviolet ray resistance is excellent, and a high transmittance is obtained at 150-180 nm.

[0013]

Said Japanese Kokai Patent Application No. Hei 6[1994]-227827 proposes a manufacturing method characterized by consisting of (1) a process that forms a porous quartz glass by flame-hydrolyzing the raw material for forming glass, (2) a process that dehydrates the porous quartz glass by heating at a temperature of 800-1,250°C, (3) a process that transforms the porous quartz glass dehydrated into a transparent glass by heating to the transparent glass formation temperature, and (4) a process that includes hydrogen in the synthetic quartz glass made transparent by heating to a temperature of 500-1,100°C in an atmosphere containing hydrogen.

[0014]

Furthermore, if the synthetic quartz glass is held in the atmosphere containing hydrogen at a high temperature, since the reduction type defects of $\equiv$Si-Si$\equiv$ and $\equiv$Si-H are easily generated, Japanese Kokai Patent Application No. Hei 8[1996]-75901 proposes a manufacturing method that forms a transparent quartz glass containing fluorine and includes hydrogen at a temperature of 500°C or less in an atmosphere containing hydrogen similarly to the method presented in Japanese Kokai Patent Application No. Hei 6[1994]-227827.

[0015]

However, these inventors reviewed the methods described in Japanese Kokai Patent Application Nos. Hei 6[1994]-227827 and Hei 8[1996]-75901; as a result, it was clarified that a sufficient ultraviolet ray resistance could not necessarily be obtained in some cases. In other words, when the porous quartz glass was heated at a high temperature of 800-1,250°C, the above-mentioned $\equiv$Si-Si$\equiv$ defect was generated. The $\equiv$Si-Si$\equiv$ defect not only generated the E' center due to the ultraviolet irradiation, but had an absorption at 245 nm and 163 nm.

[0016]

Also, even if the hydrogen treatment is applied, the $\equiv$Si-H was generated in the $\equiv$Si-Si$\equiv$ defect according to the following equation (6), and the $\equiv$Si-H generated the E' center due to the ultraviolet irradiation.

$$\equiv\text{Si-Si}\equiv + \text{H}_2 \rightarrow \equiv\text{Si-H} + \equiv\text{Si-H} \qquad (6)$$
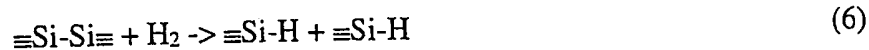
[0017]

On the other hand, in order to improve the vacuum ultraviolet transmittance, in Japanese Kokai Patent Application No. Hei 8[1996]-91867, synthetic quartz glass with an OH group concentration of 200 ppm or less, a chlorine concentration of 2 ppm or less, and a $\equiv$Si-Si$\equiv$ concentration of 1 x 10^{15} units/cm^3 or less is proposed. In Japanese Kokai Patent Application No. Hei 9[1997]-235134, synthetic quartz glass with an OH group concentration of 10-400 ppm and a concentration of the reduction type defect and the oxidation type defect of respectively 5 x 10^{16} units/cm^3 or less is proposed. In Japanese Kokai Patent Application No. Hei 7[1995]-267674, synthetic quartz glass with an OH group concentration of 100-2,000 ppm and a prescribed concentration, or less, of a transition metal, alkali metal, and alkaline-earth metal is proposed. In these conventional synthetic quartz glasses, the vacuum ultraviolet transmittance was improved by setting the OH group concentration in a prescribed range; however, a high transmittance could not necessarily be obtained in the vacuum ultraviolet region.

[0018]

Also, as a method for securing the homogeneity of the synthetic quartz glass, in Japanese Kokoku Patent No. Hei 6[1994]-27014, a method for adjusting the variation of the OH group content and the chlorine concentration by including OH groups and chlorine in the synthetic quartz glass is proposed. However, the chlorine exists in the form of $\equiv$Si-Cl in the synthetic quartz glass, and the $\equiv$Si-Cl bond has a bonding energy as weak as 7-8 eV and is easily cleaved as shown by the following equation due to the ultraviolet irradiation, so that the E' center is also generated.

$$\equiv\!Si\text{-}Cl + h\nu \rightarrow \equiv\!Si\cdot \text{ (E' center)} + Cl\cdot$$
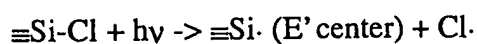
Therefore, in the methods shown in the above-mentioned literature, although excellent synthetic quartz glasses could be obtained, there was a problem with regard to the ultraviolet ray resistance.

[0019]

PROBLEMS TO BE SOLVED BY THE INVENTION

The present invention provides synthetic quartz glass that reduces the generation of an E' center, fluorescent light emission is reduced, and it has excellent ultraviolet ray resistance. The present invention provides synthetic quartz glass with excellent vacuum ultraviolet transmittance. The present invention also provides synthetic quartz glass with excellent homogeneity. In addition, the present invention provides a method suitable for manufacturing these synthetic quartz glasses.

3-1844

[0020]

MEANS TO SOLVE THE PROBLEMS

These inventors reviewed the influence of the halogen concentration in the synthetic quartz glass and the influence of an unstable structure in the synthetic quartz glass on the ultraviolet ray resistance and the ultraviolet ray transmittance in detail. As a result, it was discovered that fluorine existed in the form of $\equiv$Si-F in the synthetic quartz glass; also, the $\equiv$Si-F bond had a bonding energy as weak as 20 eV and was not cleaved by the ultraviolet irradiation, so that there was no problem with regard to the ultraviolet ray resistance. Furthermore, it was discovered that although the mechanism of the fluorine inclusion was not certain, it reduced the distorted structure of the quartz glass and improved the ultraviolet ray resistance.

[0021]

Accordingly, the present invention provides synthetic quartz glass characterized by the fact that fluorine is included, the value (I_{2250}/I_{800}) of the scattering peak intensity I_{2250} of 2250 cm^{-1} to the scattering peak intensity I_{800} of 800 cm^{-1} in a laser Raman spectrum is 1×10^{-4} or less, and the absorption coefficient of 245-nm light (hereinafter, simply the absorption coefficient of 245 nm) is 2×10^{-3} cm^{-1} or less.

[0022]

The scattering peak of 800 cm^{-1} is a peak exhibiting a $\equiv$Si-O-bond (basic vibration between silicon and oxygen), and the scattering peak of 2,250 cm^{-1} is a peak exhibiting a $\equiv$Si-H bond, which is the reduction type of defect. The value of I_{2250}/I_{800} is the index of the concentration of the $\equiv$Si-H defect ($\equiv$Si-H concentration). In the present invention, it is important that I_{2250}/I_{800} is 1×10^{-4} or less. If it is more than 1×10^{-4}, the E' center is easily generated.

[0023]

The absorption coefficient of 245 nm is also an index of the concentration of the $\equiv$Si-Si$\equiv$ defect, which is the reduction type of defect. In the present invention, it is important that the absorption coefficient of 245 nm is 2×10^{-3} cm^{-1} or less. If it is more than 2×10^{-3} cm^{-1}, the E' center is easily generated. Also, if it is more than 2×10^{-3} cm^{-1}, a high transmittance at 150-180 nm is difficult to achieve. Also, it is preferable for the absorption of light of 163 nm to be decreased. The regulation of the scattering peak of 2,250 cm^{-1} and the regulation of the absorption coefficient of 245 nm determines the amount of the reduction type of defect.

[0024]

The concentration of the E' center can be evaluated by measuring the transmittance of light of 214 nm immediately after shot-irradiating a KrF excimer laser beam by the ultraviolet-visible spectrophotometer and attaining the amount of absorption coefficient change Δk_{214} (cm^{-1}) before and after irradiating. Δk_{214} is preferably 1×10^{-1} or less, especially preferably 1×10^{-2} or less.

[0025]

When a KrF excimer laser beam is shot-irradiated, the degree of fluorescent light emission can be evaluated by measuring the fluorescent intensity L_{650} of 650 nm and the KrF excimer laser scattering light intensity S_{248} from the perpendicular direction of the incidence axis of a KrF laser beam and attaining the ratio L_{650}/S_{248} of the fluorescent intensity of 650 nm to the KrF laser (248 nm) scattering light intensity. L_{650}/S_{248} is preferably 5×10^{-4} or less, more preferably 1×10^{-4} or less.

[0026]

Also, these inventors reviewed the influence of the halogen concentration and the OH group concentration of the synthetic quartz glass on the ultraviolet ray resistance in further detail. As a result, the actions of fluorine and chlorine are different in the synthetic quartz glass. It was discovered that the chlorine existed in the form of $\equiv$Si-Cl in the synthetic quartz glass and the $\equiv$Si-Cl bond having a bonding energy as weak as 7-8 eV was easily cleaved as shown by the following equation (7) due to the ultraviolet irradiation, so that the above-mentioned E' center was generated, thereby lowering the ultraviolet ray resistance.

$$\equiv\text{Si-Cl} + h\nu \rightarrow \equiv\text{Si}\cdot(\text{E' center}) + \text{Cl}\cdot \qquad (7)$$

[0027]

Also, synthetic quartz glass containing no chlorine manufactured using a glass raw material containing no chlorine has been proposed (Japanese Kokai Patent Application No. Hei 7[1995]-291635). In the synthetic quartz glass, the fluorine concentration was set to 1,000 ppm or more to suppress the decrease in the transmittance due to the irradiation of high-energy light, and the OH group concentration was set to 50 ppm or more to suppress the absorption at 245 nm due to the oxygen deficiency type of defect $\equiv$Si-Si$\equiv$. On the other hand, the decrease in the transmittance at 150-180 nm was not mentioned, and there was a problem in using it in devices having a low-pressure mercury lamp, Xe_2 excimer lamp, F_2 laser, etc., as light sources.

[0028]

Accordingly, it was considered to be necessary to optimize the OH group, chlorine, and fluorine concentration in the synthetic quartz glass to achieve the necessary ultraviolet ray resistance improvement by suppressing the generation itself of the paramagnetic defects, and this point was further reviewed. As a result, it was discovered that when the fluorine concentration was increased and the chlorine concentration was decreased in the synthetic quartz glass, synthetic quartz glass with excellent ultraviolet ray resistance was obtained, even if the OH group concentration was slightly lowered.

[0029]

In other words, the present invention provides synthetic quartz glass in which fluorine is included, the reduction type defect is a specific amount or less, and the chlorine concentration is 100 ppm or less. In particular, as synthetic quartz glass that is effective for suppressing an unstable structure, E' center, and fluorescent light emission in synthetic quartz, synthetic quartz glass characterized by the fact that the OH group concentration is less than 50 ppm, the fluorine concentration is 100 ppm or more, the chlorine concentration is 100 ppm or less, and the hydrogen molecule concentration is 5×10^{16} molecules/cm^3 or more, is preferable.

[0030]

Also, the correlation of the influence of the halogen concentration and the hydrogen molecule concentration of the synthetic quartz glass and the influence of an unstable structure of the quartz glass was reviewed. As a result, it was discovered that if the amount of existing unstable structure was reduced by a fluorine doping and if a repair action of the paramagnetic defects due to the inclusion of the hydrogen molecules was also used, the ultraviolet ray transmittance and the ultraviolet ray resistance of the synthetic quartz glass could be improved up to a satisfactory level.

[0031]

. Accordingly, it was discovered that of the synthetic quartz glasses of the present invention, the synthetic quartz glass in which the intensity ratios I_1/I_0 and I_2/I_0 of the scattering peak intensity (I_1) of 495 cm^{-1} and the scattering peak intensity (I_2) of 606 cm^{-1}, along with the scattering peak intensity I_0 of 440 cm^{-1}, in the laser Raman spectrum were in a specific range was effective for improving the ultraviolet ray transmittance and the ultraviolet ray resistance.

[0032]

Accordingly, based on the above-mentioned knowledge, the present invention also provides synthetic quartz glass characterized by the fact that fluorine is included, the reduction type defect is a specific amount or less, and the scattering peak density (I_1) of 495 cm^{-1} and the scattering peak density (I_2) of 606 cm^{-1} in the laser Raman spectrum in relation to the scattering peak density (I_0) of 440 cm^{-1} are respectively $I_1/I_0 \leq 0.585$ and $I_2/I_0 \leq 0.136$. In particular, it is preferable to include fluorine at 100 ppm or more and hydrogen molecules at 5×10^{16} molecules/cm^3 or more.

[0033]

In the synthetic quartz glass of the present invention, the fluorine concentration is preferably 100 ppm (means weight ppm; hereinafter, the same rules correspondingly apply to the following, and ppb is similarly applied.). If the fluorine concentration is less than 100 ppm, the action of reducing the unstable structure of the synthetic quartz glass is sometimes insufficient. The fluorine concentration is more preferably 400 ppm or more, most preferably 400-3,000 ppm. If the fluorine concentration is more than 3,000 ppm, the reduction type of defect is generated, so that the ultraviolet ray resistance is likely to be lowered.

[0034]

In the synthetic quartz glass of the present invention, the OH group concentration is preferably 100 ppm or less. If it is more than 100 ppm, the transmittance in a wavelength band of about 170 nm or less is lowered and, for example, the synthetic quartz glass is likely to be not suitable for optical parts of devices having a Xe_2 excimer lamp, F_2 laser, and heavy hydrogen lamp as light sources. If the OH group concentration is 50 ppm or less, a favorable ultraviolet ray resistance is obtained, and a high transmittance is obtained in the vacuum ultraviolet region. Thus, the concentration is preferably 20 ppm or less, more preferably less than 10 ppm. In particular, the OH group concentration has an influence on the optical transmittance in the vacuum ultraviolet region of 200 nm or less, and in the synthetic quartz glass used in light in the vacuum ultraviolet region with a wavelength of 175 nm or less, the OH group concentration is preferably less than 10 ppm. Furthermore, in the synthetic quartz glass used in light in the vacuum ultraviolet region with a wavelength of 160 nm or less, the OH group concentration is preferably 5 ppm or less.

[0035]

Also, the oxygen deficiency type of defect ($\equiv Si-Si\equiv$) of the synthetic quartz glass has a large influence on the vacuum ultraviolet ray transmittance, and this oxygen deficiency type of

defect has an absorption band around a wavelength of 163 nm. The internal transmittance T_{163} (%/cm) at a wavelength of 163 nm is estimated as shown by the following equation (a[sic; i]) due to the OH group concentration C_{OH} (ppm) of the synthetic quartz glass.

$$T_{163}\ (\%/cm) \geq \exp(-0.02 C_{OH}^{0.85}) \times 100 \tag{i}$$

[0036]

However, if the oxygen deficiency type of defect exists, since there is an absorption band around 163 nm, the transmittance (T_{163}) at an actual wavelength of 163 nm is smaller than the value of the term to the right in equation (i). Furthermore, the transmittance at a wavelength of 200 nm or less is lowered, although it also depends on the size of the absorption band. Therefore, it is important not to substantially include the oxygen deficiency type of defect to obtain an excellent vacuum ultraviolet ray transmittance; it is also preferable not to substantially include the oxygen deficiency type of defect, that is, to satisfy equation (i), with respect to the internal transmittance at a wavelength of 163 nm.

[0037]

Also, in the synthetic quartz glass of the present invention, in terms of vacuum ultraviolet ray transmittance, the internal transmittance at 157 nm is preferably 70%/cm, and especially preferably 80%/cm or more.

[0038]

In the synthetic quartz glass of the present invention, the smaller the chlorine concentration, the better. If the chlorine concentration is 100 ppm or less, a favorable ultraviolet ray transmittance is obtained; the chlorine concentration is preferably 25 ppm or less in terms of homogeneity, especially preferably 10 ppm or less in terms of a favorable vacuum ultraviolet ray transmittance. Furthermore, the chlorine is preferably a very small amount, specifically 100 ppb or less, and especially preferably 50 ppb or less in terms of ultraviolet ray resistance in the vacuum ultraviolet region with a wavelength of 175 nm or less.

[0039]

In the synthetic quartz glass of the present invention, if the hydrogen molecule concentration is 5×10^{16} molecules/cm^3 or more, the action of repairing the paramagnetic defects generated by the ultraviolet irradiation is generated. In particular, the hydrogen molecule concentration is preferably 1×10^{17} molecules/cm^3 or more, more preferably 1×10^{17}-5×10^{18} molecules/cm^3, and especially preferably 5×10^{7}-5×10^{18} molecules/cm^3.

3-1844

[0040]

On the other hand, the Si-O-Si bonding angle in the $\equiv$Si-O-Si$\equiv$ bond of the quartz glass network has a certain profile. The unstable structure of the synthetic quartz glass indicates a distorted $\equiv$Si-O-Si$\equiv$ bond. Since the unstable structure of the synthetic quartz glass has a weak bonding energy, compared with a normal structure, the larger the unstable structure, the lower the vacuum ultraviolet ray transmittance. The unstable structure depends on the virtual temperature of the synthetic quartz glass and has an influence on the fluorine concentration of the synthetic quartz glass. In other words, the unstable structure can be reduced by doping fluorine into the synthetic quartz glass; because the virtual temperature is low, the unstable structure is reduced. Specifically, if the virtual temperature of the synthetic quartz glass is 1,100°C or lower, the unstable structure can be reduced, so that an excellent vacuum ultraviolet ray transmittance is obtained. In this case, the fluorine concentration is preferably 100 ppm or more. In the present invention, the virtual temperature means the virtual temperature attained using the method of A. Agarwal et al.' (J. Non-Crystl., 185, 191, 1995).

[0041]

Since metallic impurities such as alkali metals, alkaline-earth metals, and transition metals in the synthetic quartz glass of the present invention not only lower the transmittance from the ultraviolet region to the vacuum ultraviolet region, but lower the ultraviolet ray resistance, its concentration is preferably a very small amount. Specifically, the total amount of metallic impurities is preferably 100 ppb or less, especially 50 ppb or less.

[0042]

Also, in the synthetic quartz glass, since the OH group and the fluorine of the quartz glass have an influence on the refractive index, if a certain profile exists with regard to the OH group and fluorine concentrations, the homogeneity is deteriorated.

[0043]

Accordingly, it was considered to be necessary to optimize the profile of the OH group and fluorine concentrations to improve the ultraviolet ray resistance by suppressing the generation itself of the paramagnetic defects and to improve the homogeneity, and this point was reviewed. As a result, it was discovered that with the control of the profile of the fluorine concentration and the OH group concentration in a region where light is transmitted, that is, in an optical operation region, the homogeneity could be improved when the extent of the fluorine concentration and the OH group concentration was set to 15 ppm or less. Also, it was discovered that if the OH group and the fluorine had a profile in which they mutually canceled the

concentration profile in the region where light is transmitted, the homogeneity could be improved, even if the upper limit of the extent of the fluorine concentration and the OH group concentration was 25 ppm or less.

[0044]

Therefore, the present invention provides synthetic quartz glass characterized by the fact that in an optical synthetic quartz glass used by irradiating light of the ultraviolet region to the vacuum ultraviolet region, it is formed from synthetic quartz glass containing the OH group and fluorine, the extent of the OH group concentration in the optical operation region is 15 ppm or less, the extent of the fluorine concentration is 15 ppm or less, and the chlorine concentration is 25 ppm or less. Furthermore, as synthetic quartz glass with excellent homogeneity and ultraviolet ray resistance, synthetic quartz glass formed from synthetic quartz glass containing the OH group and fluorine and in which the OH group and the fluorine have a profile such that they may mutually cancel the concentration profile in the optical operation region, and in which the extent of the OH group concentration is 25 ppm or less, the extent of the fluorine concentration is 25 ppm or less, and the chlorine concentration is 25 ppm or less, is provided.

[0045]

In the present invention, the synthetic quartz glass in which both the extent of the OH group concentration and the extent of the fluorine concentration in the optical operation region are 15 ppm or less is preferable since an excellent homogeneity can be stably exerted. Also, if the OH group and the fluorine have a profile such that they may mutually cancel the concentration profile in the optical operation region, an excellent homogeneity can also be stably exerted in the synthetic quartz glass in which the extent of the OH group concentration is 25 ppm or less and the extent of the fluorine concentration is 25 ppm or less. At that time, the refractive index variation (Δn) in a plane orthogonal to incident light is preferably 20×10^{-6} or less, especially preferably 10×10^{-6} or less, more preferably 5×10^{-6} or less, and most preferably 2×10^{-6} or less. In terms of said Δn, the total of the extent of the fluorine concentration and the extent of the OH group concentration in the optical operation region is especially preferably 5 ppm or less.

[0046]

In the present invention, the optical operation region is a region where light from the ultraviolet region to the vacuum ultraviolet region are transmitted or reflected when the synthetic quartz glass is in use. Furthermore, in the present invention, the profile in which the OH group and the fluorine mutually cancel the concentration profile means a profile state in which the

fluorine concentration and the OH group concentration compensate the increase and decrease with respect to each other on an arbitrary plane orthogonal to incident light in the region where light of the synthetic quartz glass is transmitted. In other words, for example, when the fluorine concentration increases from the center to the outside of the arbitrary plane, "profile" means the state in which the OH group concentration decreases from the center to the outside of the plane, or its opposite profile state. Specifically, as shown by graphs showing the profile states of the fluorine concentration and the OH group concentration of Tables XIV-XVII in the synthetic quartz glasses of Examples 82-94 that will be mentioned later, the fluorine concentration is exhibited by a convex graph having the minimum value at the center, while the OH group concentration is exhibited by a convex group having the maximum value at the center. The concentration of both of them are in a profile state having a complementary relation or a profile state having its opposite complementary relation.

[0047]

In the present invention, as methods for manufacturing the synthetic quartz glass, the direct method, soot [transliteration] method (VAD method and OVD method), plasma method, etc., can be mentioned. The soot method is especially preferable since the manufacturing temperature is low and the mixture of impurities such as chlorine and metals can be avoided. Also, according to the soot method, the OH group is replaced with fluorine by doping the fluorine. According to the soot method, since the amount of fluorine being doped and the amount of OH group being replaced are almost equal and the OH group can be reduced without good efficiency, synthetic quartz glass with a low OH group concentration and an excellent ultraviolet ray transmittance can be obtained, [but] without good productivity.

[0048]

The method for manufacturing the synthetic quartz glass of the present invention by the soot method is explained in detail. The manufacture of the synthetic quartz glass by the soot method is a method consisting of the following processes (a), (b), and (c): (a) a process that forms a porous quartz glass by depositing and growing fine quartz glass particles, which are obtained by flame-hydrolyzing a raw material for forming quartz glass, on a base material, (b) a process that holds the porous quartz glass in an atmosphere containing fluorine and obtains a porous quartz glass containing fluorine, and (c) a process that transforms the porous quartz glass containing fluorine into a transparent glass by heating to the transparent glass formation temperature and produces a transparent quartz glass containing fluorine.

[0049]

When hydrogen molecules are included, the synthetic quartz glass is manufactured by the following processes (a), (b'), (c'), and (d), in that order.

(a) A process that forms a porous quartz glass by depositing and growing fine quartz glass particles, which are obtained by flame-hydrolyzing a raw material used to form quartz glass, on a base material,

(b') a process that holds the porous quartz glass at a temperature of 600°C or lower in an atmosphere containing fluorine and obtains a porous quartz glass containing fluorine,

(c') a process that transforms the porous quartz glass containing fluorine into a transparent glass by heating to the transparent glass formation temperature in an atmosphere not containing a substantial amount of fluorine and produces a transparent quartz glass containing fluorine, and

(d) a process that holds the transparent quartz glass containing fluorine at a temperature of 600°C or lower in an atmosphere containing hydrogen gas and produces synthetic quartz glass by including hydrogen in the transparent quartz glass containing fluorine.

[0050]

When the porous quartz glass is held in an atmosphere containing a fluorine compound, if the temperature is high, a $\equiv$Si-Si$\equiv$ defect is easily generated. In other words, if the porous quartz glass is treated at high temperature in an atmosphere containing a fluorine compound, the activation of the fluorine compound is strong, and the $\equiv$Si-Si$\equiv$ defect tends to be generated according to the following equations (8) and (9).

[0051]

$$\equiv\text{Si-O-Si}\equiv \rightarrow \equiv\text{Si-Si}\equiv \tag{8}$$
Fluorine compound
$$\equiv\text{Si-OH} \rightarrow \equiv\text{Si-F} \tag{9}$$
Fluorine compound

[0052]

. Therefore, if the porous quartz glass is treated at a low temperature of 600°C in an atmosphere containing a fluorine compound, since the activation of the fluorine compound can be suppressed and only the reaction of the above-mentioned equation (9) is caused without generating the reaction of equation (8), the $\equiv$Si-Si$\equiv$ defect is not generated.

[0053]

Next, each process is explained. In process (a), the porous quartz glass is formed by depositing and growing the fine quartz glass particles, which are obtained by supplying oxygen

gas and hydrogen gas to a multitube burner and flame-hydrolyzing the raw material used to form quartz glass, on the base material. As the raw material for forming the quartz glass, there is no particular limitation as long as it is a raw material that can be gasified; silicon halide compounds, for example, chlorides such as $SiCl_4$, $SiHCl_3$, SiH_2Cl_2, and $SiCH_3Cl_3$, fluorides such as SiF_4, $SiHF_3$, and SiH_2F_2, bromides such as $SiBr_4$ and $SiHBr_3$, and iodides such as SiI_4 or alkoxysilane represented by $R_nSi(OR)_{4-n}$ (where, R represents an alkyl group having 1-4 carbons, and n represents an integer of 0-3) can be mentioned. Also, as the above-mentioned base material, a seed rod made of quartz glass (for example, a seed rod described in Japanese Kokoku Patent No. Sho 63[1988]-24973) can be used. A sheet-shaped base material may be used without being limited to the rod shape. Also, with regard to the ratio of the oxygen gas and the hydrogen gas, since an excess hydrogen amount generates the reduction type of defect, an excess oxygen amount is preferable; specifically, the ratio of the hydrogen gas to the oxygen gas is preferably 1.6-1.9.

[0054]

Next, in process (b), the above-mentioned porous quartz glass is held at a temperature of 600°C or lower in an atmosphere containing fluorine, so that the porous quartz glass containing fluorine is obtained. As the atmosphere containing fluorine, an inert gas atmosphere containing a fluorine gas (for example, SiF_4, SF_6, CHF_3, CF_4, and F_2) at 0.1-100 vol%, especially 1-20 vol%, is preferable. Under such an atmosphere, the treatment at a temperature of 600°C or lower and a pressure of 0.1-10 atm for several tens of minutes to several hours is preferable. In particular, when the fluorine is doped at a high temperature of 500-100°C, it is preferable to suppress the generation of the reduction type of defect using an atmosphere containing 5-90 vol% of oxygen. Also, in this specification, "atm" and "Torr," which will be mentioned later, refer to absolute pressure, not gauge pressure.

[0055]

Furthermore, in process (b), since fluorine can be uniformly doped in a short time on the porous quartz glass, preferably, the compressed state (preferably 100 Torr or less, especially 10 Torr or less) is held at a prescribed temperature of 1,200°C or lower, preferably 600°C or lower, and a fluorine-containing gas is introduced up to normal pressure, so that an atmosphere containing fluorine is obtained.

[0056]

Next, in process (c), the above-mentioned porous quartz glass containing fluorine is transformed into a transparent glass by heating to the transparent glass formation temperature in

an atmosphere not containing a substantial fluorine amount, so that the transparent quartz glass containing fluorine is obtained. The transparent glass formation temperature is 1,300°C or higher, preferably 1,300-1,600°C, and especially preferably 1,350-1,500°C.

[0057]

As the atmosphere in process (c) not containing a substantial fluorine amount, there is no particular limitation as long as the fluorine-containing gas (for example, SiF_4, SF_6, CHF_3, CF_4, and F_2) is present at 0.1 vol%; a 100% inert gas atmosphere such as helium or an atmosphere mainly composed of an inert gas such as helium is preferable. The pressure may be reduced pressure or normal pressure. In particular, at normal pressure, helium gas can be used. Also, the reduced pressure is preferably 100 Torr or less, especially 10 Torr or less.

[0058]

Also, a process (e) for holding the porous quartz glass containing fluorine under reduced pressure for a prescribed time is preferably interposed between processes (b) and (c). Specifically, a process (b) for holding the porous quartz glass for several tens to minutes to several hours in an inert gas atmosphere of 100 Torr or less, preferably 10 Torr or less, is preferably included. After process (b), it is necessary to remove the fluorine from the atmosphere. Although normal pressure may be adopted, since it takes a long time, the fluorine is removed in a short time under reduced pressure like that in process (e).

[0059]

Next, in process (d), the transparent quartz glass containing fluorine obtained in process (c) is heat-treated at a temperature of 600°C or lower in an atmosphere containing hydrogen gas, so that the synthetic quartz glass is obtained. The pressure is 1-30 atm, for instance. With the hydrogen treatment at 600°C or lower, the generation of the reduction type of defects, i.e., $\equiv$Si-H and $\equiv$Si-Si$\equiv$, can be prevented. As the atmosphere containing hydrogen, an inert gas atmosphere containing 0.1-100 vol% of hydrogen gas is preferable. Furthermore, in order to control the virtual temperature, the following process (f) is preferably carried out on the transparent quartz glass.

[0060]

Process (f): The transparent quartz glass containing fluorine is held at a temperature of 800-1,100°C for 5 h or more and heat-treated by dropping to 750°C or lower at a temperature-drop rate of 10°C/h or less, so that the virtual temperature of the synthetic quartz glass is controlled. After dropping the temperature down to 750°C or lower, this level can be

maintained. In this case, the atmosphere is 100% inert gas such as helium, argon, and nitrogen, an atmosphere mainly composed of these inert gases, or a nitrogen atmosphere, and the pressure is preferably reduced pressure or normal pressure.

[0061]

Also, in order to greatly reduce the OH groups in the synthetic quartz glass of the present invention, the porous quartz glass may be dehydrated at a pressure of 1 Torr or less and a temperature of 1,000-1,300°C for a prescribed time after process (a), then heated to the transparent glass formation temperature at a pressure of 1 Torr or less, so that a transparent glass is obtained.

[0062]

The synthetic quartz glass of the present invention is used in a stepper lens and other optical parts. In order to have the necessary characteristics as optical parts, it is necessary to appropriately carry out various kinds of treatments such as homogenization, molding, and annealing (hereinafter, called optical heat treatments), and the optical heat treatments may be applied before or after process (d).

[0063]

However, since the optical heat treatments require a high temperature of 800-1,500°C, even if hydrogen is included in process (d), there is a possibility that the hydrogen molecule concentration will be lowered by the optical heat treatment thereafter. Therefore, in case the optical heat treatments are carried out after process (d), the hydrogen gas is included at 0.1-100 vol% in a pressure atmosphere of 1-30 atm. Also, when the optical heat treatments are applied after process (d), it is necessary for a furnace used for the optical heat treatments to have an explosion-proof structure. Therefore, the optical heat treatments are preferably applied before process (d).

[0064]

In the present invention, a larger amount of fluorine can be doped by also doping boron. In case boron is doped, as a boron source, BF_3, BCl_3, alkoxide of boron, etc., can be mentioned. Also, as a method for doping boron and fluorine, for example, a method that first dopes boron, then dopes fluorine can be mentioned. Specifically, for example, boron and fluorine are doped by the following method 1) or 2).

3-1844

[0065]

    1) The porous quartz glass obtained in process (a) is set in a pressurized vessel, the pressure in the vessel is decreased to about 1 Torr, and a gas containing a boron source (for example, BCl_3 vapor diluted to about 5 vol% with an inert gas such as He) is introduced. When the pressure is near normal pressure, the introduction of the above-mentioned gas containing a boron source is stopped and held for a prescribed time, so that boron is doped on the porous quartz glass. Next, fluorine is doped according to process (b).

[0066]

    2) The porous quartz glass obtained in process (a) is treated with an alkoxide vapor of boron and hydrolyzed with an alkoxide of boron in a moist atmosphere, so that fine B_2O_3 particles are precipitated in the porous quartz glass. Next, fluorine is doped according to process (b).

[0067]

    Fluorine can be doped on the porous quartz glass that is also doped with boron by the above method 1) or 2), and a larger amount of fluorine can be doped. After doping fluorine, synthetic quartz glass for optical parts can be obtained according to processes (c) and (d).

[0068]

    Also, in this case, the fluorine doping is carried out in the following sequence, for instance. An inert gas (for example, He, N_2, etc.) is introduced into the above-mentioned pressurized vessel, and the pressure is set to normal pressure. The pressure in the vessel is again reduced to about 1 Torr, and a SiF_4 gas diluted with an inert gas (for example, He, etc.) is introduced. When the pressure is near normal pressure, the introduction of the SiF_4 gas diluted with the above-mentioned inert gas is prevented and this is maintained for a prescribed time, so that fluorine is doped on the porous quartz glass containing boron.

[0069]

APPLICATION EXAMPLES

    Next, the present invention is explained in detail by application examples; however, the present invention is not limited to them. Also, synthetic quartz glasses manufactured in the following examples were evaluated by the following methods.

[0070]

(EVALUATIONS)

(Evaluation 1) Measurement of fluorine concentration

Synthetic quartz glass was heated and melted with anhydrous sodium carbonate, then distilled water and hydrochloric acid (a volume ratio of 1:1) were added to the molten solution obtained, so that a sample solution was prepared. The electromotive force of the sample solution was measured by a radiometer using each of Nos. 945-220 and 945-468 as a fluorine ion-selective electrode and a comparative electrode, and the fluorine concentration was attained based on the calibration curve prepared in advance using a fluorine-ion standard solution (Journal of Japan Chemistry, 1972(2), 350).

[0071]

(Evaluation 2) Measurement of hydrogen molecule concentration

After Raman spectroscopy, the hydrogen molecule concentration ($molecule/cm^3$) was attained by the intensity ratio ($= I_{4135}/I_{800}$) of the intensity I_{4135} detected by a scattering peak of 4,135 cm^{-1} of the laser Raman spectrum and the intensity of I_{800} of a scattering peak of 800 cm^{-1} (V.S. Khotimchenko et al., Zhurnal Prikladnoi Spektroskopii, 46(6), 987-997 (1986)). Also, the detection limit of this method is 1×10^{16} $molecules/cm^3$.

[0072]

(Evaluation 3) Measurement of OH group concentration

The OH group concentration was attained from an absorption peak at a wavelength of 2.7 μm by measurement using the infrared spectrophotometer (J.P. Williams et al., Ceram. Bull., 55(5), 524 (1976)).

[0073]

(Evaluation 4)

After Raman spectroscopy, the concentration of the ≡Si-H defect (≡Si-H concentration) was evaluated from the value (I_{2250}/I_{800}) in which the intensity I_{2250} detected from a scattering peak of 2,250 cm^{-1} of the laser Raman spectrum was divided by the intensity I_{800} of a scattering peak of 800 cm^{-1}. Here, the detection limit is $I_{2250}/I_{800} = 1 \times 10^{-4}$. A smaller value of I_{2250}/I_{800} shows a good result.

[0074]

(Evaluation 5)

Using the ultraviolet-visible-light spectrophotometer, the transmittance of light of 245 nm of a sample with a thickness of 10 mm and a sample with a thickness of 35 mm was measured, the absorption coefficient of 245 nm was calculated from their transmittance, and the existence of the generation of the $\equiv$Si-Si$\equiv$ defect was evaluated. A smaller absorption coefficient value than 245 nm shows a good result.

[0075]

(Evaluation 6) Reduction type defect

Using the vacuum ultraviolet-light spectrophotometer (VTSM-502 made by the Acton Research Co.), for samples with thicknesses of 10 mm and 4 mm, the transmittance at a wavelength of 163 nm was measured, and the absorption coefficient (k_{163}) at a wavelength of 163 nm was attained from the measured result. When the relationship with the OH group concentration (C_{OH}, the unit was ppm) included in said samples satisfied the equation $k_{163} \geq 0.02$ x $(C_{OH})^{0.85}$, it was assumed that the reduction type defect was "present," and when the relationship was not satisfied, it was assumed that the reduction type defect was "none" [[not present].

[0076]

(Evaluation 7)

Light from a KrF excimer laser (LPX-120i made by the Lambda Physics Co. [transliteration]) was irradiated onto a sample under the conditions of an energy density of 100 mJ/cm^2/pulse and a frequency of 200 Hz. Immediately after a shot irradiation of 5 x 10^6 of a KrF excimer laser beam, the transmittance at 214 nm was measured by the ultraviolet-visible-light spectrophotometer, and the absorption intensity of 214 nm due to a paramagnetic defect E' center generated by the KrF excimer laser irradiation was evaluated by the amount of absorption coefficient change Δk_{214} (cm^{-1}) before and after the irradiation. It is shown that as the value of Δk_{214} is decreased, the E' center is reduced and a good result is obtained.

[0077]

(Evaluation 8)   Evaluation of fluorescent light emission

The KrF excimer laser (LPX-120i made by the Lambda Physics Co.) was irradiated onto a sample under the conditions of an energy density of 100 mJ/cm^2/pulse and a frequency of 200 Hz. When the KrF excimer laser of a 1 x 10^6 shot was irradiated, the fluorescent light intensity L_{650} of 650 nm and the scattering light intensity S_{248} of 248 nm were respectively measured by a

fiber-induced-light spectrophotometer, and the ratio L_{650}/S_{248} of the fluorescent light intensity L_{650} of 650 nm to the scattering light intensity S_{248} of 248 nm was evaluated. It is shown that when the value of L_{650}/S_{248} is small, the fluorescent light emission is suppressed and a good result is obtained.

[0078]

(Evaluation 9) Internal transmittance of 172 nm

Using the vacuum ultraviolet spectrophotometer (VTMS-502 made by Acton Research Co.), for samples with a thickness of 10 mm and 4 mm, the internal transmittance of 172 nm was measured as the transmittance index in the vacuum ultraviolet region with a wavelength of 175 nm or less.

(Evaluation 10) Internal transmittance of 157 nm

Using the vacuum ultraviolet spectrophotometer (VTMS-502 made by Acton Research Co.), for samples with a thickness of 10 mm and 4 mm, the internal transmittance of 157 nm was measured as the transmittance index in the vacuum ultraviolet region with a wavelength of 160 nm or less, and the internal transmittance at the same wavelength was attained by the following equation.

Internal transmittance (%/cm) = $\exp(-\ln(T_1/T_2)/(d_1 - d_2)) \times 100$

Where, T_1: Transmittance (%) at a thickness of d_1 (cm)

T_2: Transmittance (%) at a thickness of d_2 (cm)

A higher transmittance is a good result.

[0079]

(Evaluation 11) An Xe_2 excimer lamp was irradiated for 3 h onto a sample with a thickness of 10 mm under the condition of 10 mW/cm^2. The transmittance at 163 nm before and after the irradiation was measured, and the transmittance change (ΔT_{163}) at 163 nm due to the irradiation was calculated. The smaller ΔT_{163}, the better the ultraviolet ray resistance.

[0080]

(Evaluation 12) Measurement of virtual temperature

The virtual temperature was measured by using the method of A. Agarwal et al.' (J. Non-Crystl., 185, 191, 1995). A quartz glass polished like a mirror was dipped into an aqueous 10% HF-2.5% H_2SO_4 solution, then polishing abrasive particles and contaminants remaining on the surface were removed. The reflection spectrum of the surface was obtained by using an infrared spectrometer (Magna 760 made by the Nikolet Co.). At that time, the angle of infrared light incidence is fixed to 6.5°, the data gap is set to about 0.5 cm^{-1}, and a 64-time scanned average

value is used. In the infrared reflection spectrum obtained in this manner, the largest peak being observed at about 1,120 cm^{-1} is due to an elastic vibration of a Si-O-Si bond of the quartz glass. If the peak position is assumed as v (cm^{-1}), the virtual temperature (T$_f$, unit: K) is attained by the following correlation equation: $v = 1114.51 + (11603.51/T_f)$.

[0081]

(Evaluation 13) Measurement of chlorine concentration

The characteristic X-ray intensity of chlorine was measured by a fluorescent X-ray analysis using kα rays of Cr, so that the chlorine concentration of the synthetic quartz glass was attained. Also, the detection limit of this method is 2 ppm.

[0082]

(Evaluation 14) Evaluation of unstable structure

With Raman spectroscopy (Ramonor T64000 made by Jobin Ybon, excitation light source: argon ion laser (a wavelength of 514.5 nm)), the intensity ratios I_1/I_0 and I_2/I_0 of the scattering peak intensity I_1 of 495 cm^{-1} and the scattering peak intensity I_2 of 605 cm^{-1}, along with the scattering peak density I_0 of 440 cm^{-1}, in the laser Raman spectrum were obtained. The smaller the intensity ratio I_1/I_0 and the intensity ratio I_2/I_0, the better.

[0083]

Also, a method for attaining each scattering peak intensity I_1, I_2, and I_0 is as follows. The scattering peak of 495 cm^{-1} and the scattering peak of 605 cm^{-1} were respectively curve-fitted by each Lorentz function and approximated so that the least squares error with an actual spectrum was the lowest, such that the coefficient of each function was determined. The scattering peak was curve-fitted by the synthesis of three Gauss functions, and the rest (base line) except for the scattering peak of 495 cm^{-1}, the scattering peak of 605 cm^{-1}, and the scattering peak of 440 cm^{-1} was curve-fitted by a quadratic function and approximated so that the least squares error with an actual spectrum was the lowest, so that the coefficient of each function was determined. The intensity of each scattering peak was attained from the above functions obtained.

[0084]

(Evaluation 15) The concentration of Na, Ca, Mg, Fe, Ni, Cu, Zn, and Ti of the synthetic quartz glass was analyzed by ICP mass spectrometry (SPQ9000 made by Seiko Instrument Co.). The detection limit of these impurities was 0.1 ppb for Ni and Cu and 0.3 ppb for the others.

[0085]

(Evaluation 16) Using a Fizeau interferometer, a helium-neon laser beam was perpendicularly irradiated onto the 200 mm ϕ surface of synthetic quartz glass sample, and the refractive index profile on the surface of 200 mm ϕ was measured.

[0086]

(Example 1) According to a well-known method, fine quartz glass particles obtained by heating and hydrolyzing (flame-hydrolyzing) $SiCl_4$, which was a raw material for forming quartz glass, in an oxyhydrogen flame were deposited and grown on a base material, so that a porous quartz glass with a diameter of 35 cm and a length of 100 cm was formed (process (a)). The porous quartz glass obtained was placed in an electric furnace whose atmosphere could be controlled, decompressed down to 10 Torr at room temperature, and held for 1 h. While introducing a mixed gas of He/SiF$_4$ = 99/1 (volume ratio), the atmosphere was held at room temperature and normal pressure for 5 h, then fluorine was doped (process (b)). The supply of SiF$_4$ was then blocked, and after holding the quartz glass in an atmosphere of 100% He for 10 h, the temperature was raised to 1,450°C in an atmosphere of 100% He. The quartz glass was made transparent by holding at this temperature for 10 h, so that a transparent quartz glass containing fluorine was obtained (process (c)).

[0087]

The transparent quartz glass containing fluorine obtained was deformed by its own weight by heating to 1,750°C or the softening point or higher in an electric furnace having a heating element made of carbon, molded into a block shape of 250 mm x 250 mm x 120 mm, and sliced into a block with a thickness of 30 mm. The block of 250 mm x 250 mm x 30 mm was held for 250 h in an atmosphere of 100% hydrogen, 10 atm, and 500°C and subjected to a hydrogen doping treatment, so that synthetic quartz glass was obtained (process (d)).

[0088]

. (Example 2) In process (b) in Example 1, the porous quartz glass was placed in the electric furnace, heated to 300°C, decompressed down to 10 Torr, and held for 1 h; a mixed gas of He/SiF$_4$ = 99/1 (volume ratio) was introduced, held at 300°C and normal pressure for 5 h in this atmosphere, and doped with fluorine. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0089]

(Example 3) In process (b) in Example 1, the porous quartz glass was placed in the electric furnace, heated to 500°C, decompressed down to 10 Torr, and held for 1 h; a mixed gas of He/SiF$_4$ = 99/1 (volume ratio) was introduced, held at 500°C and normal pressure for 5 h in this atmosphere, and doped with fluorine. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0090]

(Example 4) In process (b) in Example 1, the porous quartz glass was placed in the electric furnace, heated to 700°C, decompressed down to 10 Torr, and held for 1 h; a mixed gas of He/SiF$_4$ = 99/1 (volume ratio) was introduced, held at 700°C and normal pressure for 5 h in this atmosphere, and doped with fluorine. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0091]

(Example 5) In the process (b) in Example 1, the porous quartz glass was placed in the electric furnace, heated to 1,200°C, decompressed down to 10 Torr, and held for 1 h; a mixed gas of He/SiF$_4$ = 99/1 (volume ratio) was introduced, held at 1,200°C and normal pressure for 5 h in this atmosphere, and doped with fluorine. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0092]

(Example 6) In the process (b) in Example 1, the porous quartz glass was placed in the electric furnace, heated to 300°C, decompressed down to 10 Torr, and held for 1 h; a mixed gas of He/SiF$_4$ = 99.9/0.1 (volume ratio) was introduced, held at 300°C and normal pressure for 1 h in this atmosphere, and doped with fluorine. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0093]

(Example 7) In process (b) in Example 1, the porous quartz glass was placed in the electric furnace, heated to 300°C, decompressed down to 10 Torr, and held for 1 h; a mixed gas of He/SiF$_4$ = 99.9/0.1 (volume ratio) was introduced, held at 300°C and 300 Torr for 1 h in this atmosphere, and doped with fluorine. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0094]

(Example 8) In process (b) in Example 1, the porous quartz glass was placed in the electric furnace, heated to 300°C, decompressed down to 10 Torr, and held for 1 h; a mixed gas of He/SiF$_4$ = 99.9/0.1 (volume ratio) was introduced, held at 300°C and 100 Torr for 1 h in this atmosphere, and doped with fluorine. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0095]

(Example 9) In process (d) in Example 1, the atmosphere of 100% hydrogen, 1 atm, and a temperature of 500°C was held for 250 h, then a hydrogen doping treatment was carried out. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0096]

(Example 10) In process (d) in Example 1, the mixed gas of hydrogen/helium = 10/90 (volume ratio) was held for 250 h in an atmosphere of 1 atm and a temperature of 500°C, then a hydrogen doping treatment was carried out. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0097]

(Example 11) In process (d) in Example 1, the atmosphere of 100% hydrogen, 10 atm, and a temperature of 700°C was held for 250 h, then a hydrogen doping treatment was carried out. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0098]

(Example 12) In process (d) in Example 1, the atmosphere of 100% hydrogen, 10 atm, and a temperature of 900°C was held for 250 h, then a hydrogen doping treatment was carried out. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0099]

(Example 13) In Example 1, without applying process (b), the temperature was raised to 1,450°C in atmosphere of 100% He. The quartz glass was transformed into a transparent glass by holding at this temperature for 10 h. Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0100]

(Example 14) After process (b) in Example 1, the supply of SiF_4 was blocked, and the pressure was decreased to 1 Torr. This state was held for 1 h (process (e)). Next, 100% He was introduced, returned to normal pressure, and re-decompressed down to 1 Torr, so that an atmosphere containing no substantial fluorine amount was established. The quartz glass was transformed into to a transparent form by raising the temperature to 1,450°C in said atmosphere and holding at 1,450°C for 10 h, so that a transparent quartz glass containing fluorine was obtained (process (c)). Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0101]

(Example 15) After process (b) in Example 1, the supply of SiF_4 was blocked; the quartz glass was held for 10 h in an atmosphere of 100% He, held for 10 h in a mixed gas atmosphere of $He/SiF_4 = 99.95/0.05$ (volume ratio), heated to 1,450°C, held at 1,450°C for 10 h, and made transparent, so that a transparent quartz glass containing fluorine was obtained (process (c)). Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0102]

(Example 16) After process (b) in Example 1, the supply of SiF_4 was blocked; the quartz glass was held for 10 h in an atmosphere of 100% He, held for 10 h in a mixed gas atmosphere of $He/SiF_4 = 99.8/0.2$ (volume ratio), heated to 1,450°C, held at 1,450°C for 10 h, and made transparent, so that a transparent quartz glass containing fluorine was obtained (process (c)). Thereafter, using a method similar to that of Example 1, synthetic quartz glass was manufactured.

[0103]

The synthetic quartz glasses obtained in these Examples 1-16 were evaluated. The results of each evaluation are shown in Table I. ND represents the detection limit or less. Also, Examples 1-3, Examples 6-10, and Examples 14-15 correspond to application examples, and Examples 4-5, Examples 11-13, and Example 16 correspond to comparative examples.

[0104]

[Table I]

Table I

Example	Evaluation 1 Fluorine concentration (ppm)	Evaluation 2 Hydrogen concentration (molecules/cm^3)	Evaluation 3 OH concentration (ppm)	Evaluation 4 $\equiv$Si-H concentration (I_{2250}/I_{1800}) (-)	Evaluation 5 Absorption coefficient at 245 nm (cm^{-1})	Evaluation 6 Existence of an absorption at 163 nm	Evaluation 7 Δk_{214} [cm^{-1}]	Evaluation 8 Fluorescent light intensity ratio L_{650}/S_{248} (-)
1	896	2.9×10^{18}	2.8×10^{12}	$<1\times10^{-1}$	7.2×10^{-4}	None	8.0×10^{-3}	3.1×10^{-5}
2	983	3.0×10^{18}	3.0×10^{12}	$<1\times10^{-1}$	7.4×10^{-4}	None	8.1×10^{-3}	2.0×10^{-5}
3	1161	3.0×10^{18}	3.0×10^{12}	$<1\times10^{-1}$	7.6×10^{-4}	None	9.0×10^{-3}	2.1×10^{-5}
4	2219	2.8×10^{18}	2.8×10^{12}	$<1\times10^{-1}$	2.3×10^{-3}	Present	6.2×10^{-3}	2.5×10^{-4}
5	10412	2.9×10^{18}	2.9×10^{12}	$<1\times10^{-1}$	4.7×10^{-3}	Present	1.5×10^{-2}	1.5×10^{-4}
6	325	2.8×10^{18}	2.8×10^{12}	$<1\times10^{-1}$	7.4×10^{-4}	None	8.0×10^{-3}	6.2×10^{-5}
7	150	3.0×10^{18}	3.0×10^{12}	$<1\times10^{-1}$	7.5×10^{-4}	None	8.1×10^{-3}	1.3×10^{-4}
8	50	3.0×10^{18}	3.0×10^{12}	$<1\times10^{-1}$	7.4×10^{-4}	None	8.2×10^{-3}	2.5×10^{-5}
9	816	2.8×10^{17}	2.8×10^{17}	$<1\times10^{-1}$	7.3×10^{-4}	None	1.5×10^{-2}	3.5×10^{-5}
10	818	2.5×10^{18}	2.5×10^{18}	$<1\times10^{-1}$	7.4×10^{-4}	None	3.2×10^{-3}	3.3×10^{-5}
11	816	1.8×10^{18}	1.8×10^{18}	5.8×10^{-2}	7.2×10^{-4}	None	2.7×10^{-3}	3.3×10^{-5}
12	815	1.3×10^{18}	1.3×10^{18}	1.0×10^{-2}	7.3×10^{-4}	None	1.2×10^{-2}	3.4×10^{-5}
13	0	2.9×10^{18}	2.9×10^{12}	$<1\times10^{-1}$	7.3×10^{-4}	None	9.0×10^{-3}	9.8×10^{-5}
14	816	3.0×10^{18}	3.0×10^{12}	$<1\times10^{-1}$	7.8×10^{-4}	None	7.8×10^{-3}	2.7×10^{-5}
15	816	2.9×10^{18}	2.9×10^{12}	$<1\times10^{-1}$	7.5×10^{-3}	None	7.8×10^{-3}	3.0×10^{-5}
16	913	2.9×10^{18}	2.9×10^{12}	$<1\times10^{-1}$	2.5×10^{-3}	Present	6.5×10^{-3}	2.7×10^{-5}

[0105]

Examples 17-34 are application examples in which the influence of the OH group concentration, chlorine concentration, and fluorine concentration on the characteristics of the synthetic quartz glasses was investigated.

(Examples 17-31) According to the well-known soot method, fine SiO_2 particles formed by hydrolyzing $SiCl_4$ or $Si(CH_3O)_4$ in an oxyhydrogen flame at 1200-1500°C were deposited on a base material, so that a porous quartz glass with a diameter of 500 mm and a length of 600 mm was manufactured. The porous quartz glass was placed in an electric furnace whose atmosphere could be controlled, and a helium gas containing SiF_4 with the ratio shown in Table II was introduced under a reduced pressure of 10 Torr or less and held at normal pressure and room temperature for the time shown in Table II, so that the porous quartz glass was dehydrated and fluorine was doped. This was held under a reduced pressure of 10 Torr or less, heated to 1450°C in this state, and held at this temperature for 10 h, so that a transparent quartz glass (200 mm in diameter and 450 mm in length) was manufactured. Furthermore, the transparent quartz glass was cut to 200 mm in length and 10 mm in thickness and held at the pressure shown in Table II and 500°C for 30 h. In the above-mentioned manufacturing method, the OH group concentration and the fluorine concentration of the quartz glass were controlled by adjusting the ratio of the amount of flow of oxygen and hydrogen gases to the raw material gas during the manufacture of the porous quartz glass, or the fluorine compound concentration and the holding time during holding of the porous quartz glass in the atmosphere containing the fluorine compound. Also, the details of the manufacturing conditions (raw material used to form glass, ratio of the amount of flow of oxygen and hydrogen gases, fluorine compound concentration and pressure, and hydrogen concentration and pressure) are shown in Table II.

[0106]

[Table II]

Table II

Example	Manufacture	Raw material for forming a glass	Flame-hydrolysis conditions (the volume ratio of O2/H2 based on the raw material for forming a glass)	Fluorine doping conditions (fluorine concentration and time)		Hydrogen doping conditions (hydrogen concentration and time)	
17	Soot method	$SiCl_4$	15/25	$SiF_4/He=1/99vol\%$	10hr	$H_2=100vol\%$	10atm
18	Soot method	$SiCl_4$	15/25	$SiF_4/He=1/99vol\%$	3hr	$H_2=100vol\%$	10atm
19	Soot method	$SiCl_4$	15/25	$SiF_4/He=1/99vol\%$	2hr	$H_2=100vol\%$	10atm
20	Soot method	$SiCl_4$	15/25	$SiF_4/He=1/99vol\%$	1hr	$H_2=100vol\%$	10atm
21	Soot method	$SiCl_4$	15/25	$SiF_4/He=1/99vol\%$	30min	$H_2=100vol\%$	10atm
22	Soot method	$SiCl_4$	15/25	$SiF_4/He=1/99vol\%$	5min	$H_2=100vol\%$	10atm
23	Soot method	$SiCl_4$	15/25	No treatment		$H_2=100vol\%$	10atm
24	Soot method	$Si(CH_3O)_4$	0/0			$H_2=100vol\%$	10atm
25	Soot method	$SiCl_4$	11/30	$SiF_4/He=1/99vol\%$	3hr	$H_2=100vol\%$	10atm
26	Soot method	$SiCl_4$	13/27	$SiF_4/He=1/99vol\%$	3hr	$H_2=100v\ 1\%$	10atm
27	Soot method	$SiCl_4$	16/22	$SiF_4/He=1/99vol\%$	3hr	$H_2=100vol\%$	10atm
28	Soot method	$SiCl_4$	15/25	$SiF_4/SiCl_4/He =1/0.01/98.99vol\%$	1hr	$H_2=100vol\%$	10atm
29	Soot method	$SiCl_4$	15/25	$SiF_4/SiCl_4/He =1/0.2/99.90vol\%$	1hr	$H_2=100v\ 1\%$	10atm
30	Soot method	$SiCl_4$	15/25	$SiF_4/He=1/99vol\%$	3hr	$H_2=100vol\%$	5atm
31	Soot method	$SiCl_4$	15/25	$SiF_4/He=1/99vol\%$	3hr	$H_2/He=10/90vol\%$	1atm

3-1844

[0107]

    (Examples 32-34) According to the well-known direct method, $SiCl_4$ as a raw material for forming a glass and SiF_4 were hydrolyzed and oxidized in an oxyhydrogen flame of 1,800-2,000°C in oxygen and hydrogen gas flows using to the raw material gas at the ratios shown in Table III, so that a transparent quartz glass was directly manufactured on a base material. In the manufacturing method, the fluorine concentration of the quartz glass obtained was controlled by adjusting the mixture ratio of $SiCl_4$ and SiF_4; the OH group concentration and the hydrogen concentration were adjusted according to the ratio of the amount of oxygen and hydrogen flows. Also, the details of the manufacturing conditions (the ratio of amount of SiF_4, oxygen, and hydrogen gas flows) are shown in Table III.

[0108]

[Table III]

Table III

Example	Manufacturing method	Raw material for forming glass	Flame-hydrolysis conditions (the volume ratio of $SiF_4/O_2/H_2$ based on the raw material for forming glass)
32	Direct method	$SiCl_4$	0.8/140/200
33	Direct method	$SiCl_4$	0.8/80/800
34	Direct method	$SiCl_4$	0.0/150/200

[0109]

    The OH group concentration, chlorine concentration, fluorine concentration, and hydrogen molecule concentration of the synthetic quartz glasses manufactured in Examples 17-34 are shown in Table IV. Also, each concentration is attained by the above-mentioned methods; ND represents the detection limit or less.

[0110]

[Table IV]

Table IV

Example	OH group concentration (ppm)	Chlorine concentration (ppm)	Fluorine concentration (ppm)	Hydrogen molecule concentration (molecules/cm^3)
17	5.5	7.2	813	1.8×10^{17}
18	21	7.0	873	1.8×10^{17}
19	46	6.9	864	1.9×10^{17}
20	73	6.8	335	1.8×10^{17}
21	118	7.0	639	1.9×10^{17}
22	230	7.1	369	1.8×10^{17}
23	39	7.2	ND	1.8×10^{17}
24	21	ND	866	1.8×10^{17}
25	20	6.8	114	1.8×10^{17}
26	22	6.7	220	1.8×10^{17}
27	21	6.9	1860	1.8×10^{17}
28	21	61	873	1.8×10^{17}
29	19	134	462	1.9×10^{17}
30	21	7.0	854	5.4×10^{17}
31	20	7.1	829	1.8×10^{16}
32	950	72	1271	3.1×10^{18}
33	45	73	1293	3.1×10^{18}
34	930	68	ND	3.1×10^{16}

[0111]

· Next, for the synthetic quartz glasses manufactured in Examples 17-34, respective scattering peak intensity ratios (I_1/I_0, I_2/I_0), Δk_{214}, L_{650}/L_{248}, internal transmittance at a wavelength of 157 nm, and impurity concentration of the synthetic quartz glasses were measured and evaluated. The evaluation results are shown in Table V. Since Examples 20, 21, 22, 32, and 34 of Examples 17-34 have a high OH group concentration, Example 29 has a high chlorine concentration; Examples 23 and 34 do not include fluorine, and their characteristics are inferior to those of the other examples.

[0112]
[Table V]

Table V

Example	Evaluation 1 I_1/I_0 [-]	Evaluation 1 I_2/I_0 [-]	Evaluation 2 Δk_{157} [cm⁻¹]	Evaluation 3 L_{650}/S_{157} [-]	Evaluation 4 Transmittance at 157 nm	Evaluation 5 Impurity concentration (ppb)
17	0.560	0.123	6.03×10^{-3}	1.8×10^{-4}	78.1	All ND
18	0.560	0.123	6.05×10^{-3}	3.6×10^{-5}	54.4	All ND
19	0.560	0.123	6.13×10^{-3}	5.1×10^{-5}	35.6	All ND
20	0.559	0.123	6.03×10^{-3}	6.7×10^{-5}	24.4	All ND
21	0.562	0.124	6.05×10^{-3}	8.4×10^{-5}	14.2	All ND
22	0.564	0.125	6.07×10^{-3}	1.2×10^{-4}	4.7	All ND
23	0.589	0.138	1.56×10^{-3}	3.6×10^{-5}	39.7	All ND
24	0.561	0.123	5.98×10^{-3}	3.6×10^{-5}	54.4	All ND
25	0.568	0.129	8.84×10^{-3}	3.6×10^{-5}	55.5	All ND
26	0.566	0.128	8.16×10^{-3}	3.7×10^{-5}	53.4	All ND
27	0.543	0.115	5.48×10^{-3}	3.6×10^{-5}	54.4	All ND
28	0.560	0.123	9.38×10^{-3}	3.7×10^{-5}	54.4	All ND
29	0.570	0.128	4.03×10^{-1}	3.6×10^{-5}	56.6	All ND
30	0.561	0.124	7.56×10^{-4}	4.5×10^{-5}	54.4	All ND
31	0.562	0.124	2.43×10^{-2}	1.6×10^{-4}	55.5	All ND
32	0.516	0.101	1.51×10^{-2}	2.6×10^{-4}	<0.1	All ND
33	0.515	0.103	1.45×10^{-2}	3.6×10^{-4}	36.1	All ND
34	0.552	0.119	1.61×10^{-3}	2.5×10^{-4}	<0.1	All ND

3-1844

[0113]

Examples 35-47 are experimental examples in which the influence of I_1/I_0 and I_2/I_6 on the characteristics of the synthetic quartz glasses was investigated. (Examples 35-47) According to the well-known soot method, $SiCl_4$ was hydrolyzed in an oxyhydrogen flame, and fine SiO_2 particles formed were deposited on a base material, so that a porous quartz glass of 500 mm ϕ x 600 mm in length was manufactured (process (a)). The porous quartz glass was placed in an electric furnace whose atmosphere could be controlled; helium gas containing a fluorine compound was introduced at room temperature at a reduced pressure of 10 Torr or less until reading normal pressure. The porous quartz glass was dehydrated by holding at normal pressure and room temperature for several hours in this atmosphere, then fluorine was doped (process (b)). In a state in which the pressure was reduced to 10 Torr or less, the temperature was then raised to 1,450°C; the quartz glass was held at the temperature for 10 h, so that a transparent quartz glass (200 mm ϕ x 450 mm in length) was manufactured.

[0114]

Furthermore, the transparent quartz glass obtained was cut into 200 mm ϕ x 10 mm in thickness and held at 500°C for 30 h under the conditions shown in Table VI in an atmosphere containing hydrogen; hydrogen was doped into the quartz glass, so that synthetic quartz glasses of Examples 35-47 shown in Table VII were obtained (process (c)). In the above-mentioned manufacturing method, the OH group concentration and the fluorine concentration of the quartz glasses were controlled by adjusting the ratio of the amount of flow of oxygen and hydrogen gases to the raw material gas in process (a), and the fluorine compound concentration and the holding time in the process (b). Also, the hydrogen molecule concentration of the quartz glasses was controlled by adjusting the hydrogen concentration and the total pressure of the atmosphere in the hydrogen treatment in process (c). The details of the treatment conditions in processes (a), (b), and (c) of each example are shown in Table VI.

[0115]

[Table VI]

Table VI

	Process (a)	Process (b)	Process (c)
	Synthesis conditions (the volume ratio of O_2/H_2 based on the raw material for forming a glass)	Fluorine treatment conditions (atmosphere, treatment time)	Hydrogen treatment conditions (atmosphere, pressure)
Example 35	14/26	$SiF_4/He=1/99vol\% \cdot 5min$	$H_2=100vol\% \cdot 10atm$
Example 36	14/26	$SiF_4/He=1/99vol\% \cdot 10min$	$H_2=100vol\% \cdot 10atm$
Example 37	13/27	$SiF_4/He=1/99vol\% \cdot 30min$	$H_2=100vol\% \cdot 10atm$
Example 38	14/26	$SiF_4/He=1/99vol\% \cdot 30min$	$H_2=100vol\% \cdot 10atm$
Example 39	15/25	$SiF_4/He=1/99vol\% \cdot 3hr$	$H_2=100vol\% \cdot 10atm$
Example 40	15/25	$SiF_4/He=1/99vol\% \cdot 3hr$	$H_2=100vol\% \cdot 10atm$
Example 41	15/25	$SiF_4/He=1/99vol\% \cdot 3hr$	$H_2=100vol\% \cdot 10atm$
Example 42	16/22	$SiF_4/He=1/99vol\% \cdot 3hr$	$H_2=100vol\% \cdot 10atm$
Example 43	15/20	$SiF_4/He=1/99vol\% \cdot 3hr$	$H_2=100vol\% \cdot 1atm$
Example 44	15/25	$SiF_4/He=1/99vol\% \cdot 3hr$	$H_2/He=15/85vol\% \cdot 1atm$
Example 45	14/26	$SiF_4/He=0.5/99.5vol\% \cdot 5min$	$H_2=100vol\% \cdot 10atm$
Example 46	15/25	No treatment	$H_2=100vol\% \cdot 10atm$
Example 47	13/25	No treatment	$H_2=100vol\% \cdot 10atm$

[0116]

Next, for the samples prepared from the synthetic quartz glasses of Examples 35-47, the OH group concentration, the fluorine concentration, and the hydrogen molecule concentration were measured according to the following methods. Also, the scattering peak intensity ratios (I_1/I_0, I_2/I_0), Δk_{214}, L_{650}/L_{248}, and the internal transmittance at a wavelength of 157 nm were measured and evaluated. The evaluation results are shown in Table VII. Since Examples 45-47 of Examples 35-47 have high I_1/I_0 and I_2/I_0 ratios, their characteristics are inferior to those of the other examples.

[0117]

[Table VII]

Table VII

| | Fluorine concentration (ppm) | Hydrogen concentration (molecules/cm^3) | OH group concentration (ppm) | Evaluation 2 | | | Evaluation 3 |
				I_1 / I_0 [−]	I_2 / I_0 [−]	Δk_{211} [cm^{-1}]	Internal transmittance of 157 cm (%/cm)
Example 35	130	1.8×10^{16}	241	0.584	0.136	9.10×10^{-3}	4.3
Example 36	220	1.8×10^{12}	135	0.580	0.134	8.03×10^{-3}	11.9
Example 37	220	1.8×10^{13}	38	0.580	0.134	8.35×10^{-3}	40.4
Example 38	410	1.8×10^{16}	43	0.572	0.131	6.40×10^{-3}	37.3
Example 39	315	1.7×10^{12}	13.8	0.561	0.127	6.15×10^{-1}	63.3
Example 40	1014	1.8×10^{16}	6.8	0.557	0.125	5.98×10^{-7}	75.3
Example 41	1076	1.8×10^{13}	3.2	0.555	0.125	5.52×10^{-1}	84.3
Example 42	2274	1.8×10^{17}	1.2	0.535	0.116	5.37×10^{-2}	91.5
Example 43	1013	1.7×10^{17}	6.7	0.557	0.125	1.12×10^{-2}	75.5
Example 44	1013	1.7×10^{16}	5.6	0.557	0.125	2.29×10^{-2}	77.9
Example 45	45	1.8×10^{16}	213	0.588	0.137	1.28×10^{-2}	5.5
Example 46	0	1.8×10^{16}	198	0.590	0.138	1.62×10^{-2}	6.3
Example 47	0	1.8×10^{13}	33	0.591	0.140	1.68×10^{-2}	43.9

3-1844

[0118]

Examples 48-65 are experimental examples in which the influence of the OH group concentration and the reduction-type defect concentration on the characteristics of the synthetic quartz glasses was investigated.

(Examples 48-60) According to the well-known soot method, $SiCl_4$ was hydrolyzed in an oxyhydrogen flame; fine SiO_2 particles formed were deposited on a base material, so that a porous quartz glass of 400 mm ϕ x 600 mm in length was manufactured. The porous quartz glass was placed in an electric furnace, whose atmosphere could be controlled, then held at room temperature under a reduced pressure of 10 Torr or less, and a helium gas containing SiF_4 was introduced until reaching normal pressure. The porous quartz glass was dehydrated by holding at normal pressure and room temperature for several hours in this atmosphere. In a state in which the pressure was reduced to 10 Torr or less in an atmosphere containing no substantial fluorine amount, the temperature was then raised to 1,450°C, and the quartz glass was held at the temperature for 10 h, so that synthetic quartz glass (200 mm ϕ x 450 mm in length) was manufactured.

[0119]

Furthermore, the synthetic quartz glass obtained was cut into 200 mm ϕ x 10 mm in thickness and held for 30 h under the conditions shown in Table VIII in an atmosphere containing hydrogen; hydrogen was then doped into the synthetic quartz glass.

[0120]

In the above-mentioned manufacturing processes, the OH group concentration and the reduction-type defect concentration of the synthetic quartz glasses obtained were controlled by adjusting the volume ratio of the oxygen and hydrogen gases of the oxyhydrogen flame during the manufacture of the porous quartz glasses, as well as the concentration, treatment time, and treatment temperature of the fluorine compound during holding of the porous glasses in the atmosphere containing the fluorine compound. Also, the hydrogen molecule concentration of the synthetic quartz glasses was controlled by adjusting the treatment temperature during the hydrogen doping, the hydrogen concentration, and the total pressure of the atmosphere. The details of the treatment conditions in the processes of each example are shown in Table VIII.

[0121]
[Table VIII]

Table VIII

	Synthesis conditions (the volume ratio of O_2/H_2)	Fluorine treatment conditions (atmosphere, treatment temperature, treatment time)	Hydrogen treatment conditions (treatment temperature, atmosphere, pressure)
Example 48	1 5 / 2 5	SiF_4/He=1/99vol% · 25℃ · 10hr	500℃ · H_2=100vol% · 10atm
Example 49	1 6 / 2 2	SiF_4/He=1/99vol% · 25℃ · 10hr	500℃ · H_2=100vol% · 10atm
Example 50	1 5 / 2 5	SiF_4/He=1/99vol% · 300℃ · 5 hr	500℃ · H_2=100vol% · 10atm
Example 51	1 5 / 2 5	SiF_4/He=1/99vol% · 550℃ · 5 hr	500℃ · H_2=100vol% · 10atm
Example 52	1 5 / 2 5	SiF_4/He=1/99vol% · 700℃ · 5 hr	500℃ · H_2=100vol% · 10atm
Example 53	1 5 / 2 5	SiF_4/He=1/99vol% · 800℃ · 5 hr	500℃ · H_2=100vol% · 10atm
Example 54	1 5 / 2 5	SiF_4/He=1/99vol% · 25℃ · 5 hr	700℃ · H_2=100vol% · 10atm
Example 55	1 4 / 2 6	SiF_4/He=1/99vol% · 25℃ · 30min	500℃ · H_2=100vol% · 10atm
Example 56	1 4 / 2 6	SiF_4/He=1/99vol% · 25℃ · 10min	500℃ · H_2=100vol% · 10atm
Example 57	1 5 / 2 5	No treatment	500℃ · H_2=100vol% · 10atm
Example 58	1 5 / 2 5	SiF_4/He=1/99vol% · 25℃ · 5 hr	500℃ · H_2=100vol% · 1 atm
Example 59	1 5 / 2 5	SiF_4/He=1/99vol% · 25℃ · 5 hr	500℃ · H_2/He=15/85vol% · 1 atm
Example 60	1 5 / 2 5	SiF_4/He=1/99vol% · 25℃ · 10hr	No treatment

[0122]

(Examples 61-65) According to the soot method, $SiCl_4$ was hydrolyzed in an oxyhydrogen flame; fine SiO_2 particles formed were deposited on a base material, so that a porous quartz glass of 400 mm ϕ x 600 mm in length was manufactured. The porous quartz glass was placed in an electric furnace, whose atmosphere could be controlled, heated under reduced pressure of 1 Torr or less, held at 1,200°C for a prescribed time, heated up to 1,450°C, and held at this temperature for 10 h, so that synthetic quartz glass (200 mm ϕ x 450 mm in length) was manufactured. The synthetic quartz glass obtained was cut to 200 mm ϕ x 10 mm in thickness and held for 30 h under the conditions shown in Table IX in an atmosphere containing hydrogen, then hydrogen was doped into the synthetic quartz glass.

[0123]

In the above-mentioned manufacturing processes, the OH group concentration and the reduction-type defect concentration of the synthetic quartz glasses were controlled by adjusting the holding time at 1,200°C. Also, the hydrogen molecule concentration of the synthetic quartz glasses was controlled by adjusting the treatment temperature during the hydrogen doping, as well as the hydrogen concentration and the total pressure of the atmosphere. The details of the treatment conditions in the manufacturing processes of each example are shown in Table IX.

[0124]
[Table IX]

Table IX

	Glass formation conditions (holding time at 1,200°C)	Hydrogen treatment conditions (treatment temperature, atmosphere, pressure)
Example 61	10 hr	500°C - H_2=100vol% · 10atm
Example 62	20 hr	500°C · H_2=100vol% · 10atm
Example 63	40 hr	500°C - H_2=100vol% · 10atm
Example 64	None	500°C · H_2=100vol% · 10atm
Example 65	20 hr	No treatment

[0125]

The OH group concentration, hydrogen molecule concentration, internal transmittance at 163 nm, and existence of the reduction-type defect of the synthetic quartz glasses obtained in Examples 48-65 were attained according to the above-mentioned methods. Also, the internal transmittance of 172 nm, the internal transmittance of 157 nm, and ΔT_{163} as the ultraviolet ray resistance index were measured, then the vacuum ultraviolet ray transmittance at a wavelength of

175 nm or less, the vacuum ultraviolet ray transmittance at a wavelength of 160 nm or less, and the ultraviolet ray resistance were evaluated. Each evaluation result is shown in Tables X and XI. Since Examples 52-54 of Examples 48-65 have the reduction-type defect and Examples 55-58 and Example 64 have a relatively high OH group concentration, the internal transmittance is higher than that of the other examples.

[0126]
[Table X]

Table X

	OH group concentration (ppm)	Hydrogen molecule concentration $(molecules/cm^3)$	Internal transmittance at 163 nm (%/cm)	Existence of reduction type defect
Example 48	4.6	1.8×10^{13}	93.7	None
	2.7	1.8×10^{11}	95.0	
Example 49	5.8	1.8×10^{13}	92.3	None
	5.6	1.8×10^{11}	92.5	
Example 50	4.1	1.8×10^{11}	66.5	None
	3.8	1.8×10^{11}	15.6	
Example 51	5.8	1.4×10^{11}	84.8	None
	13.7	1.8×10^{11}	84.8	
Example 52	23.1	1.8×10^{11}	77.4	Present
	143	1.8×10^{16}	29.8	
Example 53	6.6	1.7×10^{17}	91.6	Present
	6.5	2.1×10^{16}	91.7	
Example 54	4.5		83.7	Present
	7.4		90.7	
Example 55	4.3		84.1	None
	2.8		95.6	
Example 56	53		59.4	None
	4.2		94.1	
Example 57				None
Example 58				None

Example 59				None
Example 60		Less than 5 x 10^{14}		None
Example 61		$1.8 \times 10^{1?}$ $1.8 \times 10^{1?}$		None
Example 62		$1.8 \times 10^{1?}$ $1.8 \times 10^{1?}$		None
Example 63				None
Example 64				None
Example 65		Less than 5 x 10^{14}		None

[0127]

Examples 66-81 are experimental examples in which the influence of the fluorine concentration, OH group concentration, virtual temperature, and existence of the reduction-type defect on the characteristics of the synthetic quartz glasses was investigated.

[Table XI]

Table XI

	Evaluation 1	Evaluation 2	Evaluation 3
	Internal transmittance at 172 nm (%/cm)	Internal transmittance at 157 nm (%/cm)	ΔT_{157} (%/cm)
Example 48	93.7	80.5	ND
Example 49	95.8	85.0	ND
Example 50	92.6	77.6	ND
Example 51	92.8	78.1	ND
Example 52	77.8	73.2	0.35
Example 53	48.9	20.5	0.63
Example 54	90.4	71.3	0.10
Example 55	86.1	63.6	ND
Example 56	80.0	52.5	ND
Example 57	40.5	10.9	ND
	91.8	75.9	0.01
	91.9	76.1	0.05
	93.8	80.8	0.05
	91.1	74.2	ND

Example 58			
Example 59			
Example 60			
Example 61			
Example 62			
Example 63			
Example 64			
Example 65			

[0128]

(Examples 66-81) According to the well-known soot method, $SiCl_4$ used as a material for forming glass was hydrolyzed in an oxyhydrogen flame at 1,200-1,500°C; fine SiO_2 particles formed were deposited on a base material, so that a porous quartz glass of 300 mm ϕ x 800 mm in length was manufactured. The oxyhydrogen flame conditions are shown in the process (a) of Table XII. Process (a) of Table XII shows the volume ratio of oxygen and hydrogen to $SiCl_4$ used as a raw material for forming a glass. The porous quartz glass was placed in an electric furnace whose atmosphere could be controlled; the porous quartz glass was dehydrated (OH group reduction) at the treatment temperature for the treatment time in the atmosphere shown in process (b) of Table XII, then fluorine was doped. Also, in process (b) of Table XII, the atmosphere is shown in vol%. In a state in which the pressure was reduced to 10 Torr or less, the temperature was then raised to 1,450°C; the quartz glass was held at this temperature for 10 h, so that a transparent quartz glass (105 mm ϕ x 650 mm in length) was manufactured. Furthermore, the transparent quartz glass obtained was heated to 1,750°C to the softening point or higher under 100% nitrogen gas and normal pressure in an electric furnace having a heating element made of carbon, then deformed in the growing axial direction by its own weight, so that it was molded into a columnar block. While placing the block molded in the electric furnace, this was treated at the treatment temperature for the time described in process (d) of Table XII, then dropped to room temperature in the temperature-drop profile described in process (d) of Table XII, so that the virtual temperature was controlled.

[0129]

In the above-mentioned manufacturing processes, the OH group concentration and the fluorine concentration of the synthetic quartz glasses were controlled by adjusting the ratio of the amount of flow of oxygen and hydrogen gases to the raw material gas during the manufacture of

the porous quartz glasses, as well as adjusting the atmosphere gas composition and the temperature during holding of the porus quartz glasses in the atmosphere containing a fluorine compound. Also, the virtual temperature was controlled by adjusting the temperature and the temperature-drop profile while holding the columnar blocks molded at high temperature. The OH group concentration, the virtual temperature, and the existence of the reduction-type defect of the synthetic quartz glasses obtained in each example were measured and are shown in Table XIII. Also, the internal transmittance at a wavelength of 157 nm was measured as the transmittance index in the vacuum ultraviolet region with a wavelength of 200 nm or less. The evaluation results are shown in Table XIV. Also, as shown in Tables XII-XIV, since Examples 66 and 73 of Examples 67-81 have a high OH group concentration, Example 73 has a low fluorine concentration, Example 74 has a high virtual temperature, and Example 81 has a reduction-type defect, their characteristics are inferior to those of the other examples.

[0130]

[Table XII]

Table XII

	Process (a) Synthesis conditions (the volume ratio of oxygen and hydrogen based on the raw material for forming a glass)	Process (b) Fluorine treatment conditions (atmosphere, treatment temperature, treatment time)	Annealing conditions	Process (c) (treatment temperature, treatment time, temperature drop profile)
Example 66	14／26	SiF₄/He=0.5vol%/99.5vol%, Room temperature, 3 hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 67	14／26	SiF₄/He=1vol%/99vol%, Room temperature, 15 hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 68	14／26	SiF₄/He=1vol%/99vol%, Room temperature, 20 hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 69	14／26	SiF₄/He=1vol%/99vol%, 900℃, 10hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 70	14／26	SiF₄/He=1vol%/99vol%, 500℃, 10hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 71	14／26	SiF₄/He=1vol%/99vol%, 300℃, 10hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 72	14／26	SiF₄/He=1vol%/99vol%, 300℃, 10hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 73	14／26	SiF₄/He=1vol%/99vol%, 300℃, 10hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 74	14／26	SiF₄/He=1vol%/99vol%, 300℃, 10hr		None
Example 75	14／26	SiF₄/He=1vol%/99vol%, 900℃, 10hr	1050℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 76	14／26	SiF₄/He=1vol%/99vol%, 300℃, 10hr	900℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 77	14／26	SiF₄/He=5vol%/95vol%, 500℃, 10hr	850℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 78	15／25	SiF₄/O₂/He=5vol%/20vol%/75vol%, 700℃, 10hr	850℃ × 100hr.	Temperature drop at 5°C/h down to 700°C
Example 79	15／25	SiF₄/O₂/He=5vol%/50vol%/45vol%, 900℃, 10hr	800℃ ×200hr.	Temperature drop at 5°C/h down to 700°C
Example 80	15／25	SiF₄/O₂/He=10vol%/80vol%/10vol%, 900℃, 10hr	700℃ ×200hr	
Example 81	14／26	SiF₄/He=5vol%/95vol%, 700℃, 10hr	1000℃ × 100hr.	Temperature drop at 5°C/h down to 700°C

3-1844

[0131]

[Table XIII]

Table XIII

	OH group concentration (ppm)	Fluorine concentration (ppm)	Virtual temperature [□]	Existence of reduction type defect
Example 66	17.1	150	990	None
Example 67	8.8	160	990	None
Example 68	6.4	190	990	None
Example 69	4.7	200	985	None
Example 70	3.6	200	985	None
Example 71	1.2	200	985	None
Example 72	2.5	230	980	None
Example 73	13.4	50	1010	None
Example 74	9.8	135	1140	None
Example 75	2.4	230	1040	None
Example 76	2.1	230	930	None
Example 77	1.2	460	860	None
Example 78	1.1	820	830	None
Example 79	1.1	1520	780	None
Example 80	1.1	2830	720	None
Example 81	1.2	790	990	Present

48

3-1844

[0132]

[Table XIV]

Table XIV

	Internal transmittance at 157 nm (%/cm)
Example 66	6 9 . 1
Example 67	7 3 . 9
Example 68	7 8 . 6
Example 69	8 2 . 6
Example 70	8 5 . 6
Example 71	9 4 . 0
Example 72	8 9 . 0
Example 73	6 4 . 3
Example 74	6 9 . 5
Example 75	8 6 . 7
Example 76	9 2 . 1
Example 77	9 5 . 7
Example 78	9 6 . 1
Example 79	9 6 . 6
Example 80	9 6 . 8
Example 81	8 3 . 3

[0133]

(Examples 82-85) According to the well-known direct method, $SiCl_4$ and SiF_4 were hydrolyzed and oxidized in an oxyhydrogen flame of 1,800-2,000°C, so that a 250-mm-φ transparent quartz glass was directly manufactured on a base material. The transparent quartz glass was stretched in a rod-shaped body of 200 mm φ, kneaded by the horizontal zone melting method (FZ method), and homogenized. Next, it was set in an electric furnace, held at 1,250°C for a fixed time, cooled at a cooling rate of 1°C/h down to 800°C, and held, so that synthetic quartz glass was obtained. In the above-mentioned manufacturing processes, the fluorine concentration and its profile were controlled by adjusting the mixture ratio of $SiCl_4$ and SiF_4; the OH group concentration and its profile and the hydrogen molecule concentration were adjusted by the ratio of the amount of oxygen and hydrogen flows. As a result, synthetic quartz glasses shown in Examples 82-85 of Tables XV and XVI were obtained.

3-1844

[0134]

(Examples 86-94) According to the well-known soot method, $SiCl_4$ was hydrolyzed in an oxyhydrogen flame of 1,200-1,500°C; fine SiO_2 particles formed were deposited on a base material, so that a porous quartz glass of 300 mm ϕ x 800 mm in length was manufactured. The porous quartz glass was placed in an electric furnace whose atmosphere could be controlled, then helium gas containing 1 vol% of a fluorine compound was introduced under a reduced pressure of 10 Torr or less. The porous quartz glass was dehydrated by holding at normal pressure and room temperature for several hours in this atmosphere. In a state in which the pressure was reduced to 10 Torr or less, the temperature was then raised to 1,450°C, and the quartz glass was held at the temperature for 10 h, so that a transparent quartz glass (105 mm ϕ x 650 mm in length) was manufactured.

[0135]

Furthermore, the transparent quartz glass obtained was heated to 1,750°C to the softening point or higher in an electric furnace having a heating element made of carbon, then deformed in the growing axial direction by its own weight, so that it was molded into a columnar block. While installing the block molded in the electric furnace, the temperature of the electric furnace was then dropped to 1,250°C and slowly cooled at a cooling rate of 1°C/h; when the temperature in the furnace reached 800°C, the power supply was stopped. The quartz block obtained was cut to 30 mm in thickness and held at 500°C for 240 h in an atmosphere containing hydrogen, then hydrogen was doped into the quartz glass, so that synthetic quartz glasses shown in Examples 86-94 of Tables XVI-XIX were obtained.

[0136]

In the above-mentioned manufacturing processes, the OH group concentration and the fluorine concentration of the synthetic quartz glasses were controlled by adjusting the ratio of the amount of flow of oxygen and hydrogen gases to the raw material gas during the manufacture of the porous quartz glasses, as well as adjusting the fluorine composition and the holding time during holding of the porous quartz glasses in the atmosphere containing the fluorine compound. Also, the extent of the OH group concentration and the fluorine concentration of the synthetic quartz glasses was controlled by adjusting the size during molding. Furthermore, the hydrogen molecule concentration of the synthetic quartz glasses was controlled by adjusting the conditions during the heat treatment in the atmosphere containing hydrogen.

[0137]

The fluorine concentration and its extent [variation], the OH group concentration and its extent, the chlorine concentration, and the hydrogen molecule concentration of the synthetic quartz glasses obtained in Examples 82-94 were measured.
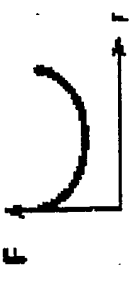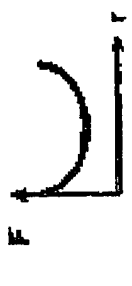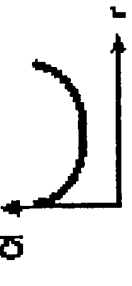
[0138]

Next, for the samples prepared from the synthetic quartz glasses of Examples 82-94, the refractive index profile, L_{650}/S_{248}, and the internal transmittance at 157 nm were measured and evaluated. The results of each evaluation are shown in Tables XV-XXI. Also, Examples 82-84, Examples 87-91, and Example 94 correspond to application examples of the present invention; the others correspond to comparative examples.
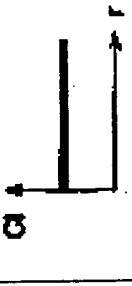
[0139]
[Table XV]

Table XV
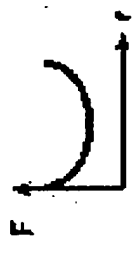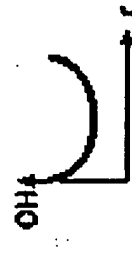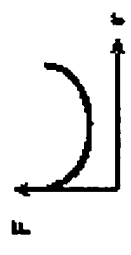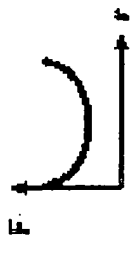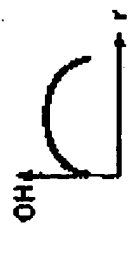
	Manufacturing method	F concentration (ppm)	OH group concentration (ppm)	Chlorine concentration (ppm)	Refractive index variation width
Example 82	Direct method	Maximum = 900 Minimum = 885 Variation width* = 15	Maximum = 950 Minimum = 935 Variation width = 15	Maximum = 23 Minimum = 14 Variation width = 9	6.5 ppm
Example 83	Direct method	Maximum = 995 Minimum = 890 Variation width = 5	Maximum = 945 Minimum = 940 Variation width = 5	Maximum = 23 Minimum = 18 Variation width = 5	2.0 ppm
Example 84	Direct method	Maximum = 893 Minimum = 891 Variation width = 2	Maximum = 943 Minimum = 941 Variation width = 2	Maximum = 23 Minimum = 20 Variation width = 3	0.7 ppm

* [Editor's note: variation width appears to mean "the value up to a certain level; in this case, up to 15 ppm"]

3-1844

[0140]
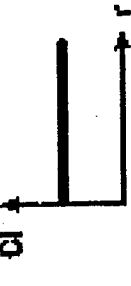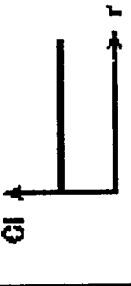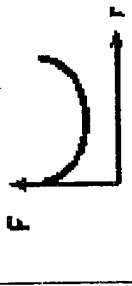
[Table XVI]

Table XVI

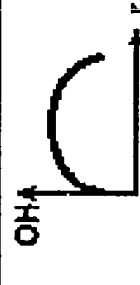|	Manufacturing method	F concentration (ppm)	OH group concentration (ppm)	Chlorine concentration (ppm)	Refractive index variation width
Example 85	Direct method	Maximum = 940 Minimum = 910 Variation width = 30	Maximum = 960 Minimum = 930 Variation width = 30	Maximum = 21 Minimum = 14 Variation width = 7	14.3 ppm
Example 86	Direct method	Maximum = 936 Minimum = 914 Variation width = 22	Maximum = 956 Minimum = 934 Variation width = 22	Maximum = 68 Minimum = 53 Variation width = 15	9.5 ppm
Example 87	Soot method	Maximum = 606 Minimum = 583 Variation width = 23	Maximum = 40 Minimum = 18 Variation width = 22	Maximum = 10 Minimum = 7 Variation width = 3	6.7 ppm

[0141]
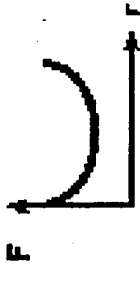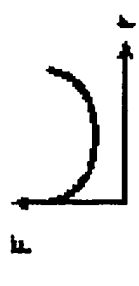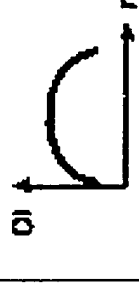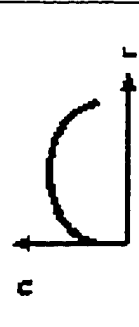
[Table XVII]
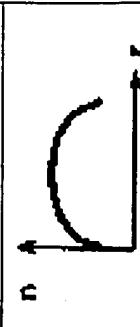
Table XVII

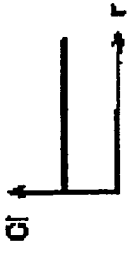|	Manufacturing method	F concentration (ppm)	OH group concentration (ppm)	Chlorine concentration (ppm)	Refractive index variation width
Example 88	Soot method	Maximum = 598 Minimum = 596 Variation width = 2	Maximum = 28 Minimum = 26 Variation width = 2	Maximum = 8 Minimum = 8 Variation width = 0	0.6 ppm
Example 89	Soot method	Maximum = 617 Minimum = 615 Variation width = 2	Maximum = 24 Minimum = 23 Variation width = 1	Maximum = 8 Minimum = 8 Variation width = 0	0.7 ppm
Example 90	Soot method	Maximum = 639 Minimum = 637 Variation width = 2	Maximum = 10.5 Minimum = 10.1 Variation width = 0.4	Maximum = 8 Minimum = 8 Variation width = 0	0.8 ppm

[0142]

[Table XVIII]

Table XVIII

	Manufacturing method	F concentration (ppm)	OH group concentration (ppm)	Chlorine concentration (ppm)	Refractive index variation width
Example 91	Soot method	Maximum = 715 Minimum = 713 Variation width = 2	Maximum = 5.6 Minimum = 5.5 Variation width = 0.1	Maximum = 8 Minimum = 3 Variation width = 0	0.8 ppm
Example 92	Soot method	Maximum = 557 Minimum = 515 Variation width = 42	Maximum = 75 Minimum = 20 Variation width = 55	Maximum = 10 Minimum = 6 Variation width = 4	10.9 ppm
Example 93	Soot method	Maximum = 634 Minimum = 592 Variation width = 42	Maximum = 58 Minimum = 31 Variation width = 28	Maximum = 10 Minimum = 6 Variation width = 4	13.6 ppm

[0143]
[Table XIX]

Table XIX

	Manufacturing method	F concentration (ppm)	OH group concentration (ppm)	Chlorine concentration (ppm)	Refractive index variation width
Example 94	Soot method	Maximum = 730 Minimum = 725 Variation width = 2 	Maximum = 3.7 Minimum = 3.6 Variation width = 0.1 	Maximum = 8 Minimum = 8 Variation width = 0 	0.8 ppm

[0144]

[Table XX]

Table XX

	Hydrogen molecule concentration (molecule/cm³)	ΔK_{2nd} [cm⁻¹]		Lcm/Scm [~]	
		Maximum	Minimum	Maximum	Minimum
Example 84	3.1×10^{19}	8.8×10^{-3}	8.8×10^{-3}	36.3×10^{-5}	36.0×10^{-5}
Example 85	3.1×10^{18}	9.1×10^{-3}	8.8×10^{-3}	36.2×10^{-6}	36.1×10^{-5}
Example 86	3.1×10^{18}	9.1×10^{-3}	8.7×10^{-3}	36.2×10^{-5}	36.1×10^{-5}
Example 87	3.1×10^{18}	8.8×10^{-4}	8.4×10^{-3}	36.5×10^{-5}	35.9×10^{-5}
Example 88	1.8×10^{18}	1.6×10^{-2}	1.6×10^{-2}	36.4×10^{-5}	35.8×10^{-6}
Example 89	1.8×10^{19}	6.1×10^{-3}	6.1×10^{-3}	6.0×10^{-6}	3.5×10^{-5}
Example 90	1.8×10^{19}	6.1×10^{-3}	6.1×10^{-3}	4.1×10^{-5}	4.0×10^{-5}
Example 91	1.8×10^{18}	6.1×10^{-3}	6.1×10^{-3}	2.5×10^{-5}	2.4×10^{-5}
Example 92	1.8×10^{18}	6.1×10^{-3}	6.1×10^{-2}	1.7×10^{-4}	1.7×10^{-5}
Example 93	1.8×10^{18}	5.9×10^{-3}	5.9×10^{-3}	8.1×10^{-5}	9.7×10^{-5}
Example 94	1.8×10^{18}	6.2×10^{-3}	6.2×10^{-3}	7.0×10^{-5}	4.8×10^{-6}
Example 95	1.7×10^{17}	6.1×10^{-3}	6.1×10^{-3}	11.0×10^{-5}	10.0×10^{-5}
Example 96	1.8×10^{18}	5.9×10^{-3}	5.9×10^{-3}	21.3×10^{-6}	21.2×10^{-3}

3-1844

[0145]

[Table XXI]

Table XXI

	Internal transmittance at 157 nm (%/cm)	
	Maximum	Minimum
Example 84	<0.1	<0.1
Example 85	<0.1	<0.1
Example 86	<0.1	<0.1
Example 87	<0.1	<0.1
Example 88	<0.1	<0.1
Example 89	58.0	39.2
Example 90	49.7	48.0
Example 91	52.6	51.6
Example 92	69.2	68.5
Example 93	78.3	78.1
Example 94	55.7	23.9
Example 95	45.5	29.6
Example 96	83.8	83.3

[0146]

EFFECT OF THE INVENTION

According to the present invention, synthetic quartz glass can be obtained, in which the ultraviolet ray transmittance is excellent, the transmittance decrease and the fluorescent light emission based on the generation of the E' center by the irradiation of high-energy light and radiation from light source such as an excimer laser are reduced, and the ultraviolet ray resistance is excellent. Also, according to the present invention, synthetic quartz glass with an excellent vacuum ultraviolet ray transmittance can be obtained. In particular, synthetic quartz glass with high transmittance can also be obtained in the vacuum ultraviolet region with a wavelength of 200 nm or less. Furthermore, according to the present invention, synthetic quartz glass with excellent homogeneity and ultraviolet ray resistance can be obtained. Therefore, the synthetic quartz glass of the present invention is very suitable for parts constituting an optical system used in light from the ultraviolet region to the vacuum ultraviolet region. Also, according to the present invention, synthetic quartz glass with excellent ultraviolet ray resistance, vacuum ultraviolet ray transmittance, and homogeneity can be easily manufactured.